Manual

for

Soil and Water

Analysis

edited by

P. Buurman, B. van Lagen and E.J. Velthorst

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BACKHUYS PUBLISHERS LEIDEN

1996

Preface

The present manual contains most of the standard analytical methods that are used at the Department of Soil Science and Geology of the Wageningen Agricultural University. Since the first version of the manual by L.Th. Begheijn, in 1982, which contained soil analyses alone, and even since the more recent (1993) versions of Soil Analyses and Water Analyses by, respectively, B. van Lagen and E.J. Velthorst, many procedures have been updated.

The decision to have this edition published commercially is due to the fact that we receive many requests for the earlier manuals, and even request for permission to publish locally, in other countries.

In this updated version, we have striven for a more complete coverage of the various analytical methods and pretreatments used in our Department. Therefore, this book contains, in addition to procedures for chemical soil and water analysis, also procedures for grain-size determination, separation of light and heavy minerals, separation of clay fractions, pretreatments for X-ray diffraction, X-ray fluorescence, and pretreatment for grain-size determination by laser-diffraction. Furthermore, we have added a chapter on the various uses of the measured properties, with an emphasis on soil formation and classification. Various authors have contributed to these sections. In addition to those credited as authors, we want to thank Mrs. N. Nakken-Brameijer and Mr. F. Lettink for their contributions to the revisions.

Because many of the texts in this book are new, they can be improved. The editors would be most grateful for comments, corrections, and additions.

Wageningen, June 1996

P. Buurman
B. van Lagen
E.J. Velthorst

Department of Soil Science and Geology
Wageningen Agricultural University
P.O. Box 37
6700 AA Wageningen, The Netherlands

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SAFETY ASPECTS

Introduction

An institution has the duty to provide a safe and healthy working place to all staff members. It is well known that laboratories are not the most healthy work environments. The presence of volatile hazardous organic liquids, explosive chemicals (e.g. perchlorate) and laboratory equipment do not guarantee optimal conditions for a safe and healthy working place. Nevertheless, it is possible to organize the laboratory environment in such a way, that normal work is possible without health problems. Laboratory staff and management must do their best to optimize laboratory conditions: laboratory staff by protecting themselves and their fellow workers, managers by creating good laboratory safety facilities. Especially the laboratory manager should realize that accidents have causes, and therefore can be prevented by a good safety program.

When an employee has become familiar and competent with a new technique, his concentration may decrease to such a point that accidents may happen. Laboratory staff should be warned, over and over again, against such an attitude. To work properly in a laboratory, all staff members should be aware of the work they do. This means, that a number of safety aspect rules must be respected.

Social behaviour is important to prevent accidents. A number of rules, listed below and elaborated upon later, can be of use as a guide to work safely in a laboratory.

Laboratory rules

- Laboratory staff should be stimulated to maintain concentration. Routine is the most common cause of laboratory accidents.

- All laboratory staff should be responsible for proper functioning of all the safety equipment. They are responsible for personal protective equipment. It should be available and used appropriately. Periodic inspections of emergency equipment, such as fire extinguishers, alarm systems, eye wash and safety showers are normal laboratory activities. Personnel must follow safety rules and be aware of safe practices.

- Annually, some time should be dedicated to training in safety techniques. There are, e.g., safety seminars, film demonstrations, and refresher courses.

- Do not keep more chemicals in the laboratory than necessary for the ongoing work. Keep the rest in a safe place such as safety cupboards.

- Always wear safety shoes, laboratory coats, and a pair of safety glasses. Don't eat and smoke in laboratories.

- Ensure that safety and precaution manuals are easy to find. They should be in the laboratory on an open bookshelf.

- Take care of fire extinguishers (water type, dry chemical type, and carbon dioxide type), fire blankets, safety showers, eye washes, safety shields, safety containers, storage facilities, chemical spill kits, laboratory fume hoods, safety wall chart, and laboratory respirators. Tenability date should be noted and replacement ordered when necessary. Take time to check regularly. Always have a first-aid kit ready.

- Used liquids or chemicals should be removed in a proper way. Follow the procedures precisely.

- Don't work alone in a laboratory. Be aware of important telephone numbers, and emergency exits.

- Check analytical procedures if they are not clear. Especially work with organic liquids may be dangerous. Be careful with electricity, gas (cylinders), and heating equipment. Work as much as possible in a fume hood. Always add acid or base to water. Don't try to catch falling glassware. Replace and remove broken glassware. Take care of all normal laboratory safety aspect rules.

- Instruct new laboratory technicians in detail.

Personal protection

Laboratory staff is usually responsable for the garments, gloves, shoes, safety glasses, etc., that they use in the laboratory. It is advisable to wear fire-retarding clothes (avoid rayon). Always wear a laboratory coat and use safety glasses when working with chemicals. Technicians should be trained in safe behaviour and should take part in yearly safety and fire excercises. A yearly safety inspection of laboratories is advisable.

Take extra precautions when radiation work has to be done. Radiation equipment should be placed in a separate room and only used by well-trained personnel. Do not let unexperienced people work with this equipment and allow no exceptions to this rule. Radiation control (medical and Geiger teller) is absolute necessary or even mandatory. Personnel have the right to know what hazardous materials are present, so inform them properly.

Improve social control in a laboratory. Each laboratory technician is responsible for the health of the others. Therefore, as a precaution, pay attention to colleagues' working habits regularly. Laboratory work with acids, bases, organic solutions etc. requires full attention from all laboratory personnel. Concentration is important, don't interrupt a working technician. Educate laboratory technicians in safe work practice. The laboratory manager must check if the work of one technician influences the safety of another.

Laboratory staff should have an annual medical examination. Through a periodic

medical exam, also shortcomings in laboratory conditions may be discovered. Depending on the type of work, a doctor may suggest immunization against, e.g., tetanus or other infections. Water and soil samples may contain microbial pathogens. Eliminate flies and other insects in the laboratory.

Be careful when new analyses are introduced. Combination of various analyses in one laboratory might give rise to an explosive mixture of gases. Maintenance of all equipment is important to prevent accidents.

Laboratory hazards

- Contact with chemicals may cause external or internal injuries. External injuries are caused by skin exposure to caustic or corrosive substances (acids, bases, reactive salts). Take care of accidents like splashes or container spills and equipment corrosion. Internal injuries may result from toxic or corrosive effects of substances absorbed by the body.

- Inorganic acids and bases have health and safety limits. Fumes can cause eye and respiratory system irritation and damage to skin and eyes. Heated acids quickly react with the skin.

- Store acids and bases separately, in well-ventilated areas and away from volatile organic and oxidizable materials. Use buckets (rubber or plastic) to transport bottles of acids and bases. Work only with strong acids and bases in a properly functioning fume hood. Slowly add acids and bases to water to avoid spattering. If skin contact is made, thoroughly flush the contaminated area with water and seek medical attention (if irritation persists). Do not rewear polluted clothing, until after it has been cleaned thoroughly. Undress if necessary; shyness is a bad advisor in this case. Leather items (shoes, belts) will retain acids and may cause severe burns.

- Perchloric acid reacts violently or explosively on contact with organic material. Don't use perchloric acid together with organic reagents, particularly volatile solvents in one fume hoods. Preferably provide a dedicated perchloric acid hood. NaOH and other chemicals produce considerable heat on dissolution, which may cause burns of skin and eyes.

- In general, consider all laboratory chemicals as hazardous and use only as prescribed. Some metals (arsenic, nickel, mercury) are highly toxic and may be carcinogenic. Avoid inhalation, ingestion, and skin contact.

- Nearly all organic solvents and reagents are hazardous. Some compounds are probably carcinogenic and should be treated with extreme caution.

- Water laboratory safety also includes (micro)biological hazards. Pathogenic micro-organisms may induce human diseases. Good laboratory safety techniques will control these agents. Even for samples of drinking water,

mouth pipetting is inadvisable, because untreated waters may contain water-borne pathogens.

- Good personal hygienic practices are important in the control of contact exposures. Disinfect hands and working surfaces frequently. Never eat or drink in the laboratory.

- Be aware of physical hazards as electrical, mechanical, and compressed gases (cylinders).

Resume

Laboratory staff often have to struggle to obtain a safe and healthy laboratory environment. Financial considerations are a common reason for the neglect of safety aspects, especially since many measures seem cost-ineffective. Still, the laboratory staff should demand that proper safety equipment is present. Because people's health may be at stake, no exceptions should be allowed to save money. Tough orders are necessary with respect to safety aspects. Guests should only enter the laboratory together with laboratory staff. Unqualified personnel has to be banned from work in the laboratory without exception. All possible measures should be taken to obtain safe and healthy working conditions.

QUALITY OF ANALYTICAL RESULTS

To attain high quality of analytical results in a laboratory, a number of principles should be adhered to. Most developments in the direction of quality in laboratories nowadays, are focussed on laboratory accreditation (Sterlab), chemometry, control charts, inter- and intra- comparison of laboratory samples, good laboratory practice (GLP), quality assurance, quality control and quality assessment. Of course, these are very important and absolute necessary to get the best results and to achieve high quality in a laboratory. For a research laboratory, like ours, the introduction of an (automatized) Laboratory Information Management System (LIMS) meets with several problems: many samples are only analyzed for one or two characteristics, and the requirements of each research project are different from the next. A LIMS would have to be tailored to such a versatile laboratory and may thus lose its effectiveness. No doubt, LIMS *can* be helpful to optimize results.

Good analytical results start with proper sampling. Soil samples are notoriously heterogeneous. In soils with irregular horizon boundaries, it may be difficult to sample a single horizon. Nevertheless, the field worker should try to obtain samples that are as homogeneous as possible. If mixed samples are taken, it would be useful to inform the laboratory staff, so that utmost care is taken to homogenize the samples before analysis. Even in seemingly homogeneous bulk samples, inadequate mixing may be a source of large errors.

Procedures for sample pretreatment, analysis, and calculation of results, have to be described accurately - and should be adhered to. Slight differences in procedures may cause large differences in results, especially between different batches of samples.

Another quality aspect is the laboratory space. It often happens that pretreatment, storage, analysis, instrumentation and calculation take place in the same room. Quality problems appear where space is insufficient, because insufficient working space always leads to variations in procedures. Sample preparation, analytical procedures, and final measurement should be in separate rooms. In case of trace element analysis, a clean, dustfree room is required for the whole procedure, because any contamination can be significant.

A well-equipped laboratory can still produce bad results if the equipment is not properly calibrated. Preventive equipment maintenance will reduce instrument malfunctioning and down-time. In addition, every analytical instrument must be calibrated to optimal sensitivity. Only data from such optimally prepared instruments are really reliable, but it often happens that data from not optimally calibrated instruments are used. Such data are sometimes revised with the aid of calculation programs in order to improve the results. This results in an overestimate of the accuracy, which may be expressed by, e.g., the number of decimals, which are not in line with the measurement accuracy.

Quality improvement can be achieved by regularly running samples in duplicate or even triplicate. This adds precision to the measurement. In addition to precision, bias is an indicator of data quality. A good laboratory should achieve low bias and high precision.

Blanks can be considered as a main factor which highly influence quality, especially in trace element analysis. Run special samples with blanks as much as possible to prevent carry-over from one to the next sample. The use of blind samples will keep the analyst alert to maintain the quality of his work.

Automation in a laboratory does increase the sample capacity, but may decrease the quality of the results. Precautions have to be taken to prevent this. Automation increases the need of careful administration, and control steps during sampling, pre-treatment, analysis and calculation are necessary to prevent mix up of samples. Sometimes, the necessary check of the obtained results is forgotten. The "black box" of automation has to be controlled too. Instrument settings must be noted to observe deviation of the analytical instrument. Use a note book with every instrument.

One of the most important factors that influence the quality of the analytical results, is the person of the analyst. Good training of an analyst is the main factor that highly benefits the quality of the analysis. An analyst should be stimulated to use an instrument to its limits, but without exceeding these limits. In addition, analysts must have sufficient background to completely understand the reasons for various operations. Involvement of the analyst in the total procedure from sampling to analytical result, including the meaning of the numbers, will increase the quality of the analytical work considerably. Interest and motivation of the analyst can be increased by sufficient knowledge of the relevant literature and by training on analytical subjects. He or she must be encouraged to "think to quality", to notice matrix effects and other possible errors. An unmotivated analyst may well be a major factor of errors and decreasing quality of results. This "quality" cannot be described statistically.

If often happens that a newly installed apparatus is directly used in the analytical cycle. Here, impatience will be counter productive, because sufficient knowledge of an instrument is an absolute necessity before it can be used properly. Of course, one wants to see returns on the investment, but without testing and optimizing its conditions, the results will be below par. Nowadays, analytical equipment is more and more sophisticated. Analytical staff must be trained well, both theoretically and practically before they start working with any new instrument. Actually, they should become specialists. In a modern laboratory, an increasing number of experts are working with highly sophisticated apparatus. So, highly-educated laboratory staff replace the old-fashioned analysts. Ideally, these new technicians should focus their attention to one or two types of apparatus. In this way quality is increased, but sickness of an expert will give problems of continuity. Laboratory management should try to get two expert operators for each piece of equipment. Therefore modern laboratories have to spend more time, money, and effort to educate their staff. Of course, education and training are expensive, but the advantage of

running more samples and attaining a higher level of quality has to be preferred. Laboratory management should be aware of a correct balance between the increased number of samples and training facilities for optimal output.

References

- Alimarin, J.P., and Yu.V. Yakovlev, 1968. Analysis of high purity materials. Israel program for scientific translations, Jerusalem, Israel.

- Dux, J.P., 1983. Handbook of quality assurance for the analytical chemistry laboratory.

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Section A

SOIL ANALYSIS

by B. van Lagen

A1: TECHNICAL REMARKS AND QUALITY

Size of sample material

The common size for the sample material is the fine earth fraction (soil fraction < 2 mm), except when mentioned otherwise in the text.

When small sample quantities (<1000 mg) have to be used for analysis, the size of the sample material should be reduced to <500 µm. This is to get a more homogeneous sample.

When very small sample quantities (<100 mg) should be used, the sample should be ground. Grinding is only permitted, when the analysis does not require natural sample material. For instance for exchange properties samples may never be ground because of changes in the surface of the particles.

Chemicals

All chemicals used in the procedures should be of analytical grade (p.a.) quality except when otherwise mentioned in the text.

The water may be demineralized water except when text indicates distilled or ultra high quality (UHQ).

Apparatus

Under the headlines "apparatus" in the procedures, only special equipment is mentioned. Standard laboratory equipment, such as glassware, is supposed to be present in any laboratory.

Quality

Every series for analysis should consist of the samples, two blanks and 1 or preferably 2 reference samples to check the performance of the analysis. The results of the reference samples should be registered on so called Shewhart-charts (Miller and Miller, 1978). When the results of these reference samples are beyond the tolerated deviation, the analysis should be repeated.

Another way to check the performance of a laboratory is to join an inter-laboratory sample exchange program.

Reference

- Miller, J.C. and J.N. Miller, 1978. Statistics for Analytical Chemistry. 2nd ed.

A2: SAMPLE PRE-TREATMENT

Principle

Commonly, a soil sample is air-dried and sieved over a 2 mm sieve before analysis. The fraction that passes through the sieve is called fine earth. If the sample contains compounds that may change upon drying, it has to be freeze-dried. When an analysis requires a small quantity of material (<1000 mg), the sample should be crushed and sieved over a 500 μm sieve. When an analysis requires a very small quantity of material (<100 mg) the sample should be ground in a ball mill.

Apparatus

Tray for sample drying
Mortar and pestle
Freeze-drier
Ball mill
Sieves of 2 mm and 500 μm

Procedure

Drying

The field sample is spread out on a tray. Leave it in a dry and dust-free place until the sample is air dry. A sample is considered dry, when the sample weight does not change more than 5% in 24 hours.

When a sample has to be freeze-dried, it is frozen first. Thereafter the sample is placed in the freeze-drier and dried according to the manufacturer's instructions.

Sieving

When the sample has been dried, it is sieved over a 2 mm sieve. The sample material left on the sieve is crushed, but **not** ground, in the mortar. Rock fragments are usually not crushed, unless a total chemistry is desired. The sieved sample is the fine earth fraction which is normally used for analysis.

Sub-sampling of fine earth can be done by machine or after careful mixing. Be aware that storage of the sample will usually result in sorting (coarse fraction on top, fine at the bottom).

When a small sample size is needed, a sub-sample is taken from the fine earth-fraction. This sub-sample is sieved over a 500 μm sieve. The material left on the sieve

is further crushed, but <u>not</u> ground, in the mortar.

When a very small sample size is needed, the sample is ground in the ball mill, until the sample size is ≤100 µm. This will take about 5 minutes of grinding.

Remarks

-   Instead of air-drying, the sample may also be dried in a drying oven. The temperature should not exceed 40° C.

-   The time of grinding the sample to a size ≤100 µm should be tested once by sieving the sample over a ≤100 µm sieve after grinding with different time intervals.

-   Some samples (e.g. volcanic soils) may not be dried because of an irreversible change of the soil. In this case the moisture content of the soils must be kept at constant level as well as possible. Storing of the sample in a plastic bag inside a well closed storage box is a good way to do this.

Reference

-   NEN 5751, 1989. Pretreatment of the sample for fysico-chemical analysis (in Dutch).

A3: MOISTURE CONTENT

Principle

The results of soil analysis are to be calculated on basis of oven-dry sample weight. Therefore the moisture-analysis is executed before any other analysis. The result on basis of the air-dry weight is multiplied with a moisture correction factor (mcf). This recalculation is not valid for analyses with a measurement directly in the obtained extract (e.g. Fe and Al fractionation and KCl exctractable ammonium and nitrate). If the additional amount of soil moisture is neglected, there will be a difference in the final result (see Fig 1.). As seen from the graph, for air dry samples (mcf <1.1) the difference between the two calculation methods is smaller than 1%, even for a low soil:extractant (S:E) ratio. For the analyses with a high S:E ratio, the final result never will be more than 1% higher if the addition of soil moisture is neglected. Especially in analyses with a low S:E ratio (KCl extractable ammonium and nitrate, P-Bray and P-Olsen) the differences will be significant. When a sample contains 100% soil moisture (mcf=2.0), the final result of an analysis with a S:E ratio of 1:5 will be 10% higher when the soil moisture is not neglected, compared to the calculation method with only using the mcf. So when an analyis contains a direct measurement in the extract, the additional soil moisture has to be included in the calculation.

Figure 1. Effect of omission of soil moisture on calculated properties.
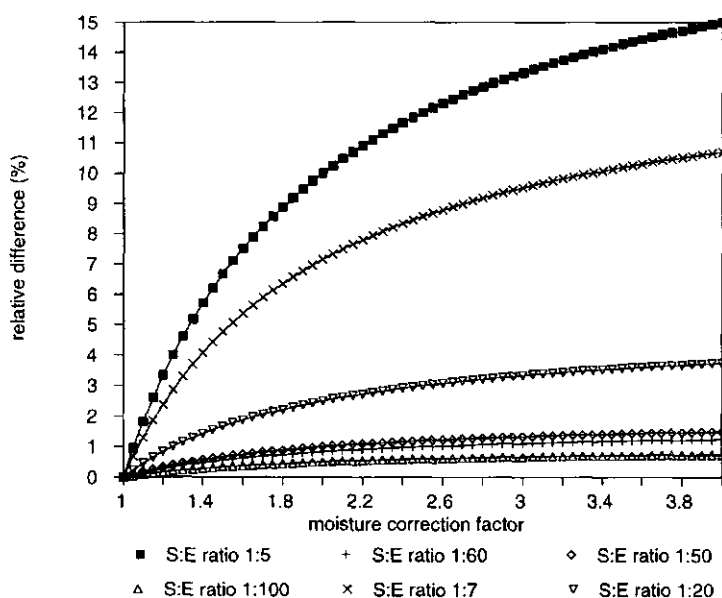
Apparatus

Drying oven
Porcelain crucible

Procedure

Place a crucible in the oven at a temperature of 105° C and leave it for at least 2 hours. Then place it in a desiccator and let it cool down to room temperature. Weigh the empty crucible (weight <u>A</u>). Weigh at least 2 g (accuracy 1 mg) of sample in the crucible and weigh it again (weight <u>B</u>). Place the crucible overnight in the oven (105° C). Transfer the crucible to the desiccator and allow to cool to room temperature. Finally weigh the crucible again (weight <u>C</u>).

Calculation

$$M \text{ (moisture content) (\%)} = \frac{(B-C) \times 100\%}{(C-A)}$$

$$mcf \text{ (moisture correction factor)} = \frac{100 + M \text{ (\%)}}{100}$$

A4: pH$_{H2O}$ and pH$_{KCl}$

Principle

The pH of the soil is measured potentiometrically in a 1:5 soil to solution suspension. The solution is either H_2O or a 1 M KCl solution.

Apparatus

Shaking machine
pH-meter with a combined electrode

Reagents

Potassium chloride (KCl)
Ampoules for buffer pH = 4, 7 and 10.

    1 M potassium chloride solution

Dissolve 74.5 g of KCl in 1 litre water.

    Buffers of pH = 4, 7 and 10

Dilute the respective ampoules according to the manufacturer's instructions.

Procedure

For air dry samples, weigh 5.0 ($\pm$ 0.05) g of sample into a 50 ml shaking bottle. Add 25 ml H_2O or 1 M KCl solution (for pH$_{H2O}$ and pH$_{KCl}$ resp.). Shake for 2 hours. Allow the suspension to settle for a few minutes. Calibrate pH-meter according to manufacturer's instructions using the correct buffers (buffers 4 and 7 for pH $\leq$ 7 and buffers 7 and 10 for pH $\geq$ 7). Measure pH of the soil in the supernatant, reading 1 decimal.

For field moist samples correct for the moisture content as follows, weigh A g of sample into a 50 ml shaking bottle. Add B ml of H_2O and shake for 2 hours. For pH$_{KCl}$ add 1.86 g of solid KCl to the soil/water mixture.

A = 5 * mcf
B = 30-A

where
mcf = moisture correction factor **(see chapter A3)**

Remarks

- After settling of the suspension some soils have a clear supernatant and some have not. When there is still a suspension measure pH in the upper part.

- Instead of a 1 M KCl solution sometimes a 0.01 M $CaCl_2$ solution is used, especially for soil fertility assessment.

- Don't keep buffers too long in storage.

- Clean the electrode regularly.

- Prepare buffer pH=10 freshly.

- Check calibration regularly during measurement.

Reference

- N.E.N. 5750, 1989. Soil- Determination of pH in soil samples (in Dutch).

<u>**A5: pH$_{NaF}$**</u>

Principle

Treating soils with fluoride, removes hydroxyl groups from the complex. The pH of the solution is measured potentiometrically. This analysis is an indication for the dominance of the amorphous substances in the adsorption complex of volcanic soils.

Apparatus

pH-meter with a combined electrode

Reagents

Sodium fluoride (NaF)
Hydrofluoric acid 48% (HF)
Ampoules for buffer pH = 7 and 10.

1 M sodium fluoride solution

Dissolve 45 g of NaF in 1 litre distilled water. Let the solution stand for two days and filter off excess NaF. Measure pH. pH should be between 7.2 and 8.1. If pH is higher add a few drops of 0.1 M HF to adjust pH.

0.1 M hydrofluoric acid

Add 3.6 ml of concentrated hydrofluoric acid to about 800 ml of distilled water. Make up to 1 litre and homogenize. **Store in a polythene bottle!!**

Buffers of pH = 7 and 10

Dilute the respective ampoules according to the manufacturer's instructions.

Procedure

Calibrate pH-meter according to manufacturer's instructions, using buffers 7 and 10. For air dry samples, weigh 1.0 (± 0.02) g of sample into a 100 ml shaking bottle. For field moist samples, weigh in A g of soil. Add 50 ml sodium fluoride solution. Shake by hands for 60 seconds. Immerse the electrode to the suspension and swirl for another 30 seconds. After another 30 seconds, measure pH, reading 1 decimal.

A = 1 * mcf

where
mcf = moisture correction factor **(see chapter A3)**

Remarks

- Don't keep buffers in storage too long.

- Clean the electrode regularly.

- Prepare buffer pH=10 freshly.

- Check calibration regularly during measurement.

References

- Mizota, C., and L.P. Van Reeuwijk. 1989. Clay mineralogy and chemistry of soils formed in volcanic material in diverse climatic regions. Soil Monograph 2. International Soil Reference and Information Centre, Wageningen. 186 pp.

- Van Reeuwijk, L.P., 1992. Procedures for Soil Analysis. I.S.R.I.C. Technical Paper 9, 3rd ed., page 6-2.

A6: TOTAL or ORGANIC CARBON and TOTAL NITROGEN (elemental analyzer)

Principle

Carbon and nitrogen in the sample is oxidized in an oxidation column at high temperature. The formed nitrogen oxide is reduced by copper to N_2. The mixture of CO_2 and N_2 is separated by gaschromatography and detected by thermal conductivity detector (T.C.D.). This method is known as the "flash combustion" technique. Optionally carbonate is removed by HCl before the analysis.

Apparatus

Elemental analyzer
Micro-balance
Tin capsules (8 x 5 mm)
Silver capsules (12½ x 5 mm)
Aluminium block with place for capsules
Micro-pipette for 40 µl
Hot plate

Reagents

Acetanilide (C_8H_9ON)
Magnesium perchlorate anhydrous ($Mg(ClO_4)_2$)
Quartz wool
Hydrochloric acid 37% (HCl)

10 % hydrochloric acid

Add about 300 ml water to a 500 ml measuring cylinder and carefully add 135 ml HCl 37%. Allow to cool, make up to volume with distilled water and homogenize.

Procedure

Standards:

Weigh 0 to 3 mg (accuracy of 1 µg) of acetanilide into a capsule (tin for non-calcareous samples and silver for calcareous samples). Weigh in at least 4 portions of acetanilide with different weights. Close the capsule and transfer it to the sampler of the elemental analyzer.

Organic and inorganic carbon and nitrogen:

Weigh 15 to 20 mg (accuracy of 1 µg) of ground sample into a tin capsule, using the micro-balance. Close the capsule and transfer it to the sampler of the elemental analyzer.

Organic carbon and total nitrogen for calcareous samples:

Weigh 15 to 20 mg (accuracy of 1 µg) of ground sample into a silver capsule using the micro-balance. Place the capsule in the aluminium block. Add 40 µl of 10% HCl using the micro-pipette. Allow to stand overnight. The next day add another 40 µl of 10% HCl. Allow to stand for about 4 hours. Place the aluminium block on the hot plate. Warm the block to a temperature of 65° C. Let the samples dry for about 3 hours. Allow to cool. Close the capsule and transfer it to the sampler of the elemental analyzer.

Measurement

Measure carbon and nitrogen according to the manufacturer's instructions using the instrumental settings of table 1. The formed H_2O is trapped by a column filled with $Mg(ClO_4)_2$.

Table 1: Instrumental setting for carbon and nitrogen measurement by elemental analyzer

Parameter	Total carbon	Organic carbon
Oven temperature of oxidation column	1020° C	1070° C
Oven temperature of reduction column	650°C	650°C
Oven temperature of gaschromatograph	60° C	60° C
Filament temperature	190° C	190° C
Cycle time	360 seconds	360 seconds
Sampler open after	10 seconds	10 seconds
Sampler closed after	15 seconds	15 seconds
Oxygen injection during	40 seconds	40 seconds
Peak enabling	30 seconds	30 seconds
Helium flow	±90 ml min^{-1}	±90 ml min^{-1}
Purge flow	40 ml min^{-1}	40 ml min^{-1}
Oxygen flow	20 ml min^{-1}	20 ml min^{-1}

Calculation

The calculation is done by the management software of the system. This software prepares a graph of the absolute carbon or nitrogen weight against the peak area of the respective peak. The peak area of the samples is recalculated to the absolute weight of carbon or nitrogen. The percentage is calculated from this absolute carbon or nitrogen weight in relation to the weight of the sample. These results finally have to be corrected for the moisture content by multiplying them with the moisture correction factor.

Remarks

- When the calcareous samples have cooled down and the samples have to be stored overnight, this is best done in a desiccator.

- The volume of 40 µl 10% HCl is enough to neutralize ± 6 mg of $CaCO_3$. That means that samples with $CaCO_3$-concentrations of 50% or less can be treated as described above. Samples with more than 50% have to be treated once again with 40 µl 10% HCl.

- Carbonate can be estimated by subtracting organic carbon from total carbon and recalculating this difference to carbonate.

- A quartz tube, closed at the bottom with a piece of quartz wool, is inserted to the oxidation column to prevent clogging of the column with the oxidized mineral material of the soils.

References

- Eager 200 Instruction Manual.

- Instruction Manual EA 1108 Elemental Analyzer.

- Nieuwenhuize, J., Y.E.M. Maas and J.J. Middelburg, 1994. Rapid analysis of organic carbon and nitrogen in particulate materials. Marine Chemistry 45:217-224.

A7: ORGANIC CARBON (wet oxidation)

Principle

The organic carbon in the sample is oxidized with a mixture of potassium dichromate and sulphuric acid without external heating. The excess potassium dichromate is titrated with ferrous sulphate. This method is known as the Walkley-Black method.

Apparatus

Dispenser for 25 ml
Dispenser for 10 ml
Burette
Magnetic stirrer

Reagents

Potassium dichromate ($K_2Cr_2O_7$)
Sulphuric acid 96% (H_2SO_4)
Phosphoric acid 85% (H_3PO_4)
Ferrous sulphate ($FeSO_4.7H_2O$)
Diphenylamine-4-sulfonic acid barium salt ($C_{24}H_{20}BaN_2O_6S_2$)

   0.1667 M potassium dichromate

Dissolve 49.04 g $K_2Cr_2O_7$ in approx. 800 ml water. Transfer to a 1 litre volumetric flask. Make up to volume with demineralized water and homogenize.

   1 M (approx.) ferrous sulphate

Dissolve 278 g $FeSO_4.7H_2O$ in ca. 800 ml water and add 15 ml concentrated H_2SO_4. Transfer to a 1 litre volumetric flask. Make up to volume with water and homogenize.

   0.16% diphenylamine-4-sulfonic acid barium salt (indicator)

Dissolve 0.4 g diphenylamine-4-sulfonic acid barium salt in 250 ml of water.

Procedure

Weigh 1 g (accuracy 1 mg) of sample into a 500 ml wide-mouth conical flask. Pipette 10 ml of the potassium dichromate solution. Add 20 ml concentrated sulphuric acid using the dispenser. Swirl the flask carefully and allow to stand for 30 minutes. Add 200 ml water and allow to cool. Then add 10 ml phosphoric acid using the dispenser. Add 2 ml of the indicator-solution and titrate with ferrous sulphate while stirring

magnetically. The colour changes from brown to purple to blue and finally to green. The last change of colour is very abrupt. For the titration, more than 6 ml of ferrous sulphate should be used. If the amount is lower, repeat the analysis using less sample (see remark).

Calculation

$$\text{Organic Carbon (\%)} = \frac{10}{B} \times \frac{(B-V) \times 0.39 \times mcf}{W}$$

where

B   = ml ferrous sulphate used for blank
V   = ml ferrous sulphate used for sample
10/B   = molarity of ferrous sulphate
mcf   = moisture correction factor
W   = sample weight (g)
0.39   = conversion factor (including a correction factor for a supposed 70% oxidation of organic carbon)

Remarks

-        Execute the oxidation in a fumeboard!

-        The oxidation in this method is not complete. It is estimated, that only 70% of the organic matter will be oxidized. Therefore the result of the analysis is recalculated to 100% oxidation.

-        If more than 40% of the dichromate is used for oxidation, there is a possibility that the oxidation is far less than 70%. Therefore the analysis has to be repeated, when less than 6 ml of the ferrous sulphate solution is used for the titration.

-        The blank is also used to determine the molarity of the ferrous sulphate, therefore preferably 3 blanks should be included.

-        It is difficult to dissolve diphenylamine-4-sulfonic acid barium salt. So prepare this solution 1 day before using it.

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References

- Nelson, D.W. and L.E. Sommers, 1982. Total carbon, organic carbon and organic matter. in: Methods of Soil Analysis. Part 2 - Chemical and Microbiological Properties. Agronomy No. 9, 2nd ed., page 539-579.

- Van Reeuwijk, L.P., 1992. Procedures for Soil Analysis. I.S.R.I.C. Technical Paper no. 9, 3rd ed., page 5-1 and 5-2.

A8: TOTAL NITROGEN (wet oxidation)

Principle

The sample is digested in a mixture of sulphuric acid and selenium. The formed ammonium is measured colorimetrically as an emerald green complex of ammonium with sodium salicylate, sodium nitroprusside and sodium hypochlorite using an auto analyzer.

Apparatus

Dispenser for 10 ml
Kjeldahl digestion unit
Centrifuge
Auto analyzer for ammonium

Reagents

Sulphuric acid 96% (H_2SO_4)
Selenium mixture according to Wieninger
Sodium hydroxide 32% (NaOH), special grade for ammonium determination
Sodium potassium tartrate ($NaKC_4H_4O_6.4H_2O$)
Sodium phosphate, dibasic ($Na_2HPO_4.2H_2O$)
Sodium salicylate ($NaC_7H_5O_3$)
Sodium nitroprusside ($Na_2Fe(CN)_5NO.2H_2O$)
Sodium hypochlorite (NaOCl)
Ammonium sulphate (($NH_4)_2SO_4$)
Hydrochloric acid 37% (HCl)
Brij-35 wetting agent

      20% sodium hydroxide stock solution

Carefully add 625 ml sodium hydroxide 32% to 350 ml water. Allow to cool and make up to 1 litre with distilled water. Homogenize.

      20% sodium potassium tartrate stock solution

Dissolve 200 g sodium potassium tartrate in 1 litre water. Homogenize.

      stock buffer-solution

Dissolve 89 g sodium phosphate, dibasic in 800 ml hot water. Allow to cool. Add 50 ml 32% sodium hydroxide solution. Allow to cool. Make up to 1 litre with water and homogenize.

working buffer solution

Combine 200 ml stock buffer solution and 250 ml Na,K-tartrate stock solution. Swirl. Add 60 ml 20% sodium hydroxide stock solution. Swirl and allow to cool. Make up to 1 litre with water, add 1 ml Brij-35 and homogenize.

sodium salicylate/sodium nitroprusside solution

Dissolve 150 g sodium salicylate and 300 mg sodium nitroprusside in 800 ml water. Make up to 1 litre with water and homogenize. Filter through a folded filter and add 1 ml Brij-35. Mix. **Store in a dark bottle.**

sodium hypochlorite

Add 5.0 ml sodium hypochlorite to 80 ml water. Make up to 100 ml with water and add 2 drops of Brij-35. Homogenize. **Prepare fresh daily.**

1 M hydrochloric acid

Add 80 ml hydrochloric acid 37% to 800 ml water. Allow to cool and make up to 1 litre with water. Homogenize.

5,000 $mmol(+)m^{-3}$ ammonium stock-solution

Weigh 330.0 mg ammonium sulphate (dried at 105°C) into a 150 ml beaker and dissolve in 100 ml water. Transfer to a 1 litre volumetric flask. Make up to volume with water and homogenize.

Standard series

Add 200 ml of water and 3 drops 1 M HCl to a 250 ml volumetric flask. Pipette 25 ml 5,000 $mmol(+)m^{-3}$ ammonium stock solution to the flask. Make up to volume with water and homogenize. This solution is now 500 $mmol(+)m^{-3}$ ammonium (=standard 7).
Add to 50 ml volumetric flasks a few ml of water and 1 drop of 1 M HCl. Pipette respectively: 0, 5, 10, 20, 30, and 40 ml of the 500 $mmol(+)m^{-3}$ ammonium standard to the flask. Make up to volume with water and homogenize. The standard series is now:
Standard 1:   0 $mmol(+)m^{-3}$ NH_4^+
Standard 2:   50 $mmol(+)m^{-3}$ NH_4^+
Standard 3:   100 $mmol(+)m^{-3}$ NH_4^+
Standard 4:   200 $mmol(+)m^{-3}$ NH_4^+
Standard 5:   300 $mmol(+)m^{-3}$ NH_4^+
Standard 6:   400 $mmol(+)m^{-3}$ NH_4^+
Standard 7:   500 $mmol(+)m^{-3}$ NH_4^+

Procedure

digestion

Weigh 1 g of sample (accuracy 1 mg) in a digestion tube. Add 500 mg selenium

mixture. Add 5 ml sulphuric acid using a dispenser and place the tube in the digestion unit. Turn the heating equipment to about 400° C. Continue heating till the mixture is transparent. Take the tube off the heating assembly and allow to cool gently. Add very carefully a few drops of water and again allow to cool. Repeat this procedure until there is no further reaction because of the addition of water to the sulphuric acid. Transfer the solution to a 100 ml centrifuge tube and centrifuge for 10 minutes at 3000 rpm. Transfer the supernatant to a 200 ml volumetric flask and wash the residue another time with about 50 ml of water. Centrifuge again for 10 minutes at 3000 rpm and transfer the supernatant to the same volumetric flask. Make the flask up to volume with water and mix thoroughly.

Measurement

Dilute the sample 5 times with water and measure the ammonium content using the auto analyzer.
Prepare the auto analyzer for measurement following the manufacturer's instructions (for flow scheme see Figure 1). Wavelength is 660 nm, flowcell is 1.5 cm. Fill the autosampler with standards and samples. Run automatically at a speed of 30 samples per hour. Calculate concentrations of the samples with standards. Run blanks regularly to check the baseline. If the sample is beyond the calibration range dilute more and if the sample is below standard 2, dilute less.

Calculation

$$\textit{total nitrogen (\%)} = \frac{(C-B) \times D \times 0.28 \times mcf}{W}$$

where

C   = concentration ammonium for sample $(mmol(+)m^{-3})$
B   = concentration ammonium for blank $(mmol(+)m^{-3})$
D   = dilution factor
W   = sample weight (mg)
mcf = moisture correction factor
0.28 = conversion factor

Remarks

-    Use distilled water throughout this procedure.

-    Make sure that the fumes of sulphuric acid are sucked off with the suction assembly of the digestor.

- Work in a fume cupboard.

- Be very careful, when adding the water to the acid!!

- Weigh in less material, when the sample is rich in organic matter (>10%)

- Take care of the sodium hydroxide, because it is very etching.

- Take special grade 32% NaOH-solution for ammonium determination.

- Sodium nitroprusside is toxic.

- Keep sodium hypochlorite in a refrigerator.

References

- Begheijn, L.Th., 1980. Methods of Chemical Analyses for Soils and Waters. Dept. of Soil Science and Geology, Agricultural University Wageningen, 3rd ed., page 20-21.

- Manual of Tecator digestion system 6/12, (1981).

- Velthorst, E.J., 1993. Manual for Chemical Water Analyses. Dept. of Soil Science and Geology, Wageningen Agricultural University.

Figure 2. Flow scheme for ammonium determination

AMMONIUM

tube colour

to sampler wash receptacle

grn/grn (2.00) water

blk/blk (0.32) air

gry/gry (1.00) working buffer solution

orn/grn (0.10) sample

blk/blk (0.32) Na-salicylate/Na-nitroprusside solution

orn/yel (0.16) Na-hypochlorite solution

yel/yel (1.20) from flow cell

flow rates in ml/min

waste

37°C
7.7 ml

waste

to flow cell

colorimeter
flow cell: 15 mm
filter : 660 nm
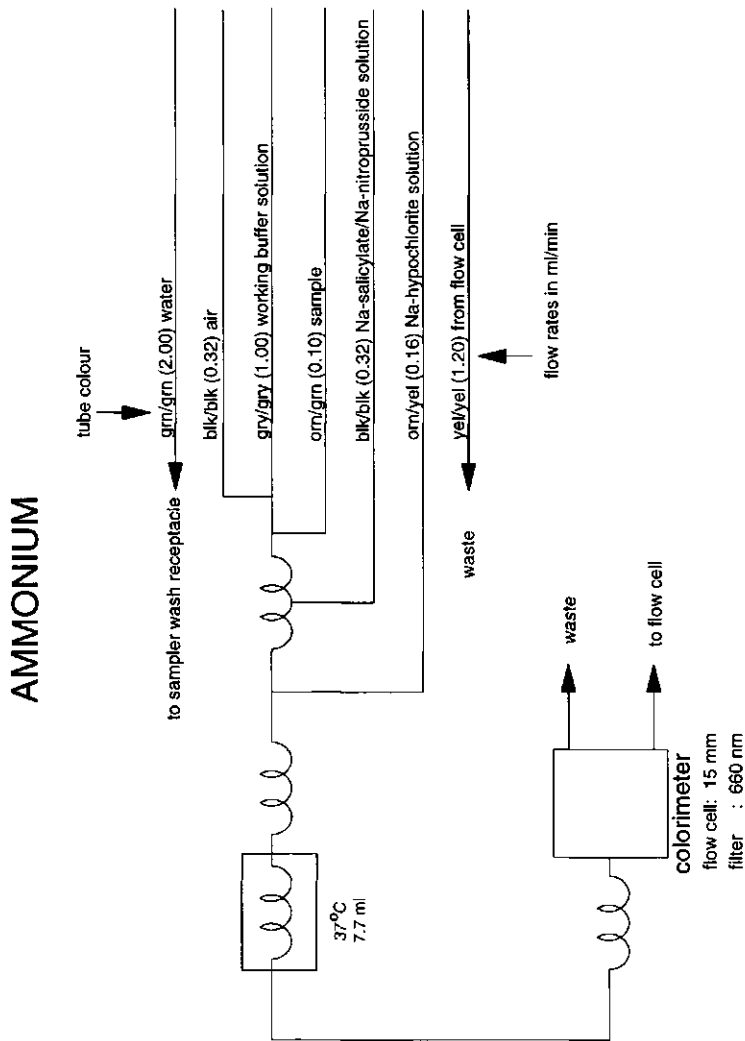
A9: CARBONATE

Principle

Carbonate in the sample is dissolved in an excess of hydrochloric acid. The remainder of the acid is titrated with sodium hydroxide. This method is known as the Piper method. Because not only calcite is dissolved but also other carbonates, the result is also known as the calcium carbonate equivalent.

Apparatus

Shaking machine
Burette
pH meter with a combined electrode
Magnetic stirrer

Reagents

Hydrochloric acid 37% (HCl)
Calcium carbonate ($CaCO_3$)
Ampoule for 0.25 M NaOH
Ampoules for pH buffers 4 and 7

 1 M hydrochloric acid

Add about 800 ml water to a 1000 ml measuring cylinder and carefully add 86 ml HCl 37%. Allow to cool, make up to volume with water and homogenize.

 0.25 M sodium hydroxide

Dilute an ampoule according to manufacturer's instructions.

 buffers for pH 4 and 7

Dilute the respective ampoules according to manufacturer's instructions.

Procedure

Weigh 5 g of soil into a 250 ml shaking bottle. Instead of a reference sample also 500 mg $CaCO_3$ may be used as reference. Add 100.0 ml 1 M HCl using a pipette and swirl gently. Place the cap on the bottle but don't close it tightly.
Let it stand overnight. Close the shaking bottle and shake for 2 hours. Let the suspension settle.

Calibrate the pH meter according to the manufacturer's instructions. Pipette 5 ml of the supernatant to a 150 ml beaker and add 20 ml of water. Add a magnetic stirring rod and place the beaker on the stirrer. Bring the electrode into the solution. Titrate to end-point pH=7.5 with the 0.25 M NaOH solution. Check pH calibration regularly.

Calculation

$$CaCO_3\ (\%) = \frac{(B-V)\times t \times 100 \times mcf}{W}$$

where

B	= ml NaOH used for blank
V	= ml NaOH used for sample
t	= molarity NaOH
W	= sample weight (g)
mcf	= moisture correction factor
100	= conversion factor

Remarks

- If pH_{H2O} < 7 no carbonate is expected.

- When a low concentration of carbonate (<10%) is expected, 0.2 M HCl may be used instead of 1 M. The NaOH-titration solution should then be 0.1 M instead of 0.25 M.

- Instead of a burette and a pH meter, an automatic titrator may be used.

- Take care of CO_2 contamination, when preparing the NaOH solution. Use fresh distilled water and close the burette with a CO_2- trap.

- Instead of a pH meter, also a 0.1 % phenolphthalein indicator solution may be used to detect the end-point. For this dissolve 100 mg of phenolphthalein in 100 ml ethanol (96%). The colour will change from transparent to purple.

- Not only carbonates are dissolved in hydrochloric acid but also some minerals may dissolve. When this happens the carbonate content is over-estimated.

References

-       Allison, L.E. and C.D. Moodie, 1965. Carbonate. in: Methods of Soil Analysis. Part 2 - Chemical and Microbiological Properties. Agronomy No. 9 page 1379-1396.

-       Van Reeuwijk, L.P., 1992. Procedures for Soil Analysis. I.S.R.I.C. Technical Paper no. 9, 3rd ed., page 7-1 and 7-2.

A10: GYPSUM

Principle

Gypsum ($CaSO_4.2H_2O$) in the sample is dissolved in water and precipitated by acetone. The precipitate is dissolved again with water. The calcium of the gypsum is measured by atomic absorption spectrophotometry (A.A.S.).

Apparatus

Dispenser for 100 ml
Shaking machine
Centrifuge
Drying oven
A.A.S.

Reagents

Calcium sulphate (gypsum) ($CaSO_4.2H_2O$)
Hydrochloric acid 37% (HCl)
Barium chloride ($BaCl_2.2H_2O$)
Acetone (2-propanone) (C_3H_6O)
Lanthanum oxide (La_2O_3)
Ampoule for 1000 mg L^{-1} Ca

      1 M hydrochloric acid

Add about 200 ml water to a 250 ml measuring cylinder and carefully add 22 ml HCl 37%. Allow to cool, make up to volume with demineralized water and homogenize.

      1 M barium chloride

Dissolve 60 g $BaCl_2.2H_2O$ in 250 ml water.

      5% lanthanum-solution

Weigh 58.6 g lanthanum oxide into a 1 litre beaker. Add about 800 ml water and carefully add 100 ml HCl 37%. Allow the lanthanum oxide to dissolve. Allow to cool and transfer to a 1 litre measuring cylinder. Make up to volume with water and homogenize. If needed, filtrate over a folded filter.

      2% lanthanum-solution

Bring 100 ml 5% lanthanum-solution to a 250 ml measuring cylinder. Add 50 ml 1 M HCl and make up to 250 ml with water. Homogenize.

1000 mg L^{-1} Ca-stock solution

Dilute an ampoule for 1000 mg L^{-1} Ca according to manufacturer's instructions.

Standard series

Pipette 5 ml 1000 mg L^{-1} Ca-stock solution into a 100 ml volumetric flask. Make up to volume with water and homogenize. This solution is now 50 mg L^{-1} Ca.
Pipette from this solution respectively 0, 5, 10 and 20 ml into 50 ml volumetric flasks. Add 10 ml 5% lanthanum-solution to each flask. Make up to volume with water and homogenize.The standard series is now:
Standard 1:   0.0 mg L^{-1} Ca
Standard 2:   5.0 mg L^{-1} Ca
Standard 3: 10.0 mg L^{-1} Ca
Standard 4: 20.0 mg L^{-1} Ca

Procedure

extraction

Weigh 10 g (accuracy 0.1 g) of sample into a 250 ml shaking bottle. Instead of a reference sample, 100 mg $CaSO_4.2H_2O$ may be used as reference. Add 100 ml water by dispenser. Shake overnight. Transfer 35 ml of the suspension to a 50 ml centrifuge tube and centrifuge for 15 minutes at 3500 rpm. Pipette 3 ml of the clear supernatant to a test tube and add 10 drops 1 M HCl. Add 2 ml 1 M $BaCl_2$-solution. If the solution is getting turbid proceed with washing and measurement. If no turbidity appears there is no gypsum in the extract.

washing

Pipette 20 ml of the extract to a 50 ml centrifuge tube. Add 20 ml acetone and homogenize. Allow to stand for 10 min. Centrifuge for 10 minutes at 2500 rpm. Decant the clear supernatant. Wash the residue with 10 ml acetone. Again centrifuge for 10 minutes at 2500 rpm and decant the supernatant. Place the tube in a drying oven at ± 50° C. Take good care of good ventilation in the oven and in the room where this oven stands. Take the tube out of the oven and allow to cool. Pipette 40 ml water in the tube and redissolve the precipitate. Dilute 5 ml of this solution with 5 ml of the 2% lanthanum-solution. Homogenize.

Measurement

Measure Ca with the A.A.S. at 422.7 nm. If the sample is out of the calibration range dilute more. Make sure that the lanthanum concentration in the measuring solution is 1%

Calculation

$$Gypsum\ (\%) = \frac{(C-B) \times D \times mcf \times 0.08592}{W}$$

where

C   = Ca concentration in sample (mg L^{-1})
B   = Ca concentration in blank (mg L^{-1})
D   = dilution factor (2 is standard)
mcf   = moisture correction factor
W   = sample weight (g)
0.08592   =conversion factor

Remarks

-       The precipation with acetone is specific for gypsum.

-       The maximum solubility of gypsum at 20° C is 2.41 g L^{-1} water. Therefore if the soil contains 2% or more gypsum repeat the analysis with a different soil/water ratio.

-       Use transparent centrifuge tubes (e.g. a glass tube) if possible, so that you can see if the supernatant is clear and if the precipitate is redissolved.

References

-       Van Reeuwijk, L.P., 1992. Procedure for Soil analysis. I.S.R.I.C. Technical Paper 9, 3rd ed., page 8-1 and 8-2.

-       Weast, R.C., 1974-1975. Handbook of Chemistry and Physics. 55th ed. CRC Press, Cleveland, Ohio.

A11: EXCHANGEABLE BASES AND CATION EXCHANGE CAPACITY (CEC)

Principle

The exchangeable bases are removed with an excess of Ba. Thereafter, if the CEC also has to be measured, the soil is brought to an ionic strength of about 0.01 M. Then the Ba is removed with an excess of $MgSO_4$. The Mg lost for the exchange with Ba is measured to determine the CEC. The exchangeable bases and the magnesium are measured with atomic absorption and atomic emission spectroscopy (AAS and AES). CEC can alternatively be calculated as the sum of the exchangeable bases and the exchangeable acidity **(see chapter A12)**. This is also known as the effective CEC. This is one of the possible methods to measure the CEC. Others are mentioned in Section G.

Apparatus

Shaking machine
Centrifuge
Centrifuge tubes with screw caps
A.A.S./A.E.S.
Diluter

Reagents

Barium chloride ($BaCl_2.2H_2O$)
Magnesium sulphate ($MgSO_4.7H_2O$)
Lanthanum oxide (La_2O_3) or Lanthanum chloride ($LaCl_2.7H_2O$)
Hydrochloric acid 37% (HCl)
Cesium chloride (CsCl)
Ampoules for 1000 mg L^{-1} Ca, Mg, K and Na

      0.1 M barium chloride

Dissolve 24.4 g $BaCl_2.2H_2O$ in water and transfer it to a 1 litre volumetric flask. Make up to volume with demineralized water and homogenize.

      0.0025 M barium chloride

Pipette 25 ml of the 0.1 M $BaCl_2$ solution into a 1 litre volumetric flask and make up to volume with water. Homogenize.

      0.02 M magnesium sulphate

Dissolve 4.9296 g $MgSO_4.7H_2O$ in water and transfer it to a 1 litre volumetric flask. Make up to volume with water and homogenize.

1 M hydrochloric acid

Add about 800 ml water to a 1 litre measuring cylinder and carefully add 86 ml HCl 37%. Allow to cool and make up to volume with water. Homogenize.

5% lanthanum-solution

Weigh 58.6 g La_2O_3 into a 1 litre beaker. Add about 800 ml water and then carefully add 100 ml HCl 37%. Allow the lanthanum to dissolve. (Alternatively weigh in 133.7 g of $LaCl_2.7\ H_2O$ and add 10 ml HCl 37%). Allow to cool and transfer it to a 1 litre measuring cylinder. Make up to 1 litre with water and homogenize. If needed filtrate over a folded filter.

1.11% lanthanum-solution

Transfer 222 ml of the 5% lanthanum solution to a 1 litre measuring cylinder. Add 600 ml 1 M HCl and make up to volume with water. Homogenize.

10000 mg L^{-1} cesium solution

Weigh 12.7 g CsCl into a 150 ml beaker. Dissolve in 100 ml water. Transfer the solution to a 1 litre measuring cylinder and add 27 ml concentrated HCl. Make up to 1 litre with water. Homogenize.

1250 mg L^{-1} cesium solution

Transfer 62.5 ml of the 10000 mg L^{-1} Cs-solution to a 500 ml measuring cylinder. Make up to 500 ml with water and homogenize.

1000 mg L^{-1} standard solutions of Ca, Mg, K and Na

Dilute the respective ampoules according to manufacturer's instructions.

Standard series

Ca and Mg

Pipette 10 ml 1000 mg L^{-1} Mg stock solution to a 100 ml volumetric flask. Make up to volume with water and homogenize. This solution is now 100 mg L^{-1} Mg.
Pipette 5 ml 1000 mg L^{-1} Ca stock solution into a 100 ml volumetric flask. Pipette 5 ml of the 100 mg L^{-1} Mg solution to the same volumetric flask. Make up to volume with water and homogenize. The mixed solution is now 50 mg L^{-1} Ca and 5 mg L^{-1} Mg.
Pipette from this mixed solution respectively 0, 5, 10 and 20 ml into 50 ml volumetric flasks. Add 10 ml 5% lanthanum-solution and 5 ml 0.1 M $BaCl_2$ to each flask. Make up to volume with water and homogenize.The standard series is now:
Standard 1:   0.0 mg L^{-1} Ca and 0.00 mg L^{-1} Mg
Standard 2:   5.0 mg L^{-1} Ca and 0.50 mg L^{-1} Mg
Standard 3: 10.0 mg L^{-1} Ca and 1.00 mg L^{-1} Mg
Standard 4: 20.0 mg L^{-1} Ca and 2.00 mg L^{-1} Mg
(1 mg L^{-1} = 1 ppm)

Na and K

Pipette 5 ml 1000 mg L^{-1} Na-stock solution to a 500 ml volumetric flask. Pipette 10 ml 1000 mg L^{-1} K-stock solution in the same volumetric flask. Make up to volume with water and homogenize.
This mixed solution is now 10 mg L^{-1} Na and 20 mg L^{-1} K.
Pipette from this mixed solution respectively 0, 5, 10 and 20 ml into 50 ml polypro-pylene volumetric flasks. Add 5 ml 10000 mg L^{-1} cesium-solution and 10 ml 0.1 M $BaCl_2$ to each flask. Make up to volume with water and homogenize. The standard series is now:
Standard 1: 0.0 mg L^{-1} Na and 0.0 mg L^{-1} K
Standard 2: 1.0 mg L^{-1} Na and 2.0 mg L^{-1} K
Standard 3: 2.0 mg L^{-1} Na and 4.0 mg L^{-1} K
Standard 4: 4.0 mg L^{-1} Na and 8.0 mg L^{-1} K

Mg for CEC

Pipette 10 ml 1000 mg L^{-1} Mg-stock solution to a 100 ml volumetric flask. Make up to volume with water and homogenize. This solution is now 100 mg L^{-1} Mg.
Pipette 5 ml of the 100 mg L^{-1} Mg-solution to a 100 ml volumetric flask. Make up to volume with water and homogenize. The solution is now 5 mg L^{-1} Mg.
Pipette from this solution respectively 0, 5, 10 and 20 ml into 50 ml volumetric flasks. Add 10 ml 5% lanthanum-solution to each flask. Make up to volume with water and homogenize. The standard series is now:
Standard 1: 0.00 mg L^{-1} Mg
Standard 2: 0.50 mg L^{-1} Mg
Standard 3: 1.00 mg L^{-1} Mg
Standard 4: 2.00 mg L^{-1} Mg

Procedure

Exchange of bases

Weigh 2.5 g of soil (accuracy of 1 mg) into a 50 ml centrifuge tube with screw cap. Weigh the tube with the soil (weight **FW**). Add about 30 ml of the 0.1 M $BaCl_2$ solution and shake for 1 hour. Centrifuge for 10 minutes at 2500 rpm. Decant the supernatant into a 100 ml volumetric flask. Repeat the shaking and centrifugation step two times. Every time, decant the supernatant into the same volumetric flask of 100 ml. Fill the volumetric flask to the mark with 0.1 M $BaCl_2$ and homogenize. In this solution (I) the exchangeable bases are measured.
Add 30 ml 0.0025 M $BaCl_2$ to the soil in the centrifuge tube and shake overnight. (The concentration of the $BaCl_2$ now should be about 0.01 M). Centrifuge for 10 minutes at 2500 rpm and decant the supernatant. This supernatant is not needed for analysis. Again weigh the tube with the soil (weight **SW**).
Add 30 ml of the 0.02 M $MgSO_4$-solution to the soil and shake for 2 hours.

Centrifuge for 10 minutes at 2500 rpm and decant the supernatant over a coarse filter in an erlenmeyer flask. Stopper the flask. In this filtrated solution (**II**) the CEC is measured.

Measurement

exchangeable Ca and Mg

Dilute the extraction solution (**I**) 1+9 with the 1.11 % lanthanum-solution. Measure with the A.A.S. The wavelength for the Ca-measurement is 422.7 nm and for the Mg-measurement 285.2 nm. If the dilution of 10 times is not enough, dilute the extract again, but make sure that the matrix of the solution is 0.01 M $BaCl_2$, 1% lanthanum and 0.8 M HCl.

exchangeable Na and K

Dilute the extraction solution (**I**) 1+4 with the 0.63 % cesium-solution. Measure with the A.E.S. The wavelength for the Na-measurement is 589.0 nm and for the K-measurement 766.5 nm. If the dilution of 5 times is not enough, dilute the extract again, but make sure that the matrix of the solution is 0.02 M $BaCl_2$ and 1000 mg L^{-1} cesium.

Mg for CEC

Pipette 1 ml of the CEC-extract (**II**) into a 250 ml volumetric flask. Add 50 ml of the 5% lanthanum solution. Make up to volume with water and homogenize. Measure with the A.A.S. The wavelength for the Mg-measurement is 285.2 nm.

Calculation

Exchangeable bases

$$\text{Exchangeable cations (cmol(+) } kg^{-1} \text{ soil)} = \frac{(C-B) \times D \times mcf \times 10}{W \times E}$$

where

B = concentration of cation in blank (mg L^{-1})
C = concentration of cation in sample (mg L^{-1})
D = dilution factor (standard is 10 for Ca and Mg; 5 for Na and K)
mcf = moisture correction factor
W = sample weight (g)
E = equivalentmass of respective cation

$$E_{Ca} = 20.04$$
$$E_{Mg} = 12.16$$
$$E_{Na} = 22.99$$
$$E_{K} = 39.10$$

CEC

$$CEC \ (cmol(+) \ kg^{-1} \ soil) = \frac{(B-C) \times (30 + SW - FW) \times 2.056 \times mcf}{W}$$

where

B   = concentration of magnesium in blank (mg L^{-1})
C   = concentration of magnesium in sample (mg L^{-1})
FW   = first weight of tube with sample (g)
SW   = second weight of tube with sample (g)
mcf   = moisture correction factor
W   = sample weight (g)
2.056 = conversion factor

Remarks

-    If only the exchangeable bases are to be measured, there is no need to weigh the tubes. The procedure may be concluded then after the last extraction for the exchangeable bases.

-    The results are given in SI-units; cmol(+) kg^{-1} is equivalent to the formerly used meq 100 g^{-1}.

-    This method should not be used for soils with allophane, because sulphate is adsorbed at the complex. For allophane containing soils we recommend to determine the ECEC.

-    For ECEC in the exchangeable bases extract (0.1 M $BaCl_2$ extract) also aluminium and total acidity can be measured (see also Chapter G).

References

-    Gilman, G.P., 1979. A proposed method for the measurement of exchange properties of highly weathered soils. Australian Journal of Soil Research 17:129-139.

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-   Perkin Elmer, 1976. Analytical Methods for Atomic Absorption Spectrophotometry.

-   Velthorst, E.J. and B. van Lagen, 1992. Optimisation of Na and K measurement with AES. Intern verslag no 56. Department of Soil Science and Geology, Agricultural University, Wageningen (in Dutch).

A12: EXCHANGEABLE ACIDITY

Principle

The acid cations (Al^{3+} and H^+) of the adsorption-complex are exchanged with an excess of KCl. The extract is titrated to measure the total exchangeable acidity. Exchangeable Al is measured by atomic absorption spectrometry (A.A.S.) using a nitrous oxide/acetylene flame. The difference between total exchangeable acidity and exchangeable Al is the exchangeable H^+.

Apparatus

Shaking machine
Dispenser for 50 ml
Centrifuge
Centrifuge tube with screw cap
Burette
pH-meter with combined electrode
A.A.S. with a nitrous oxide/acetylene burner

Reagents

Potassium chloride (KCl)
Ampoule for 0.01 M NaOH
Ampoules for buffers pH 4 and 7
Hydrochloric acid 37% (HCl)
Ampoule for 1000 mg L^{-1} aluminium

     1 M potassium chloride

Dissolve 74.6 g KCl in 1 litre of demineralized water.

     0.01 M NaOH

Dilute an ampoule for 0.01 M NaOH according to manufacturer's instructions.

     buffers for pH 4 and 7

Dilute the respective ampoules according to the manufacturer's instructions.

     1000 mg L^{-1} aluminium stock solution

Dilute an ampoule for 1000 mg L^{-1} aluminium according to the manufacturer's instructions.

1 M hydrochloric acid

Add about 800 ml water to a 1000 ml measuring cylinder and carefully add 86 ml HCl 37%. Allow to cool and make up to volume with water. Homogenize.

Standard series

Pipette 20 ml of the 1000 mg L^{-1} Al stock solution into a 100 ml volumetric flask. Make up to volume with water and homogenize. This standard solution is 200mg.L^{-1} Al.

Pipette 0, 5, 15 and 25 ml of the 200 mg L^{-1} standard solution into 100 ml volumetric flasks. Add 2 drops of 1 M HCl and 7.5 g of solid KCl to each flask. Let the KCl dissolve and fill each flask to the mark with water and homogenize. The standard series is now:

Standard 1: 0 mg L^{-1} Al^{3+}
Standard 2: 10 mg L^{-1} Al^{3+}
Standard 3: 30 mg L^{-1} Al^{3+}
Standard 4: 50 mg L^{-1} Al^{3+}

Procedure

extraction with 1 M KCl

Weigh 5 g (accuracy 0.01 g) of sample into a 50 ml centrifuge tube with screw cap. Add 30 ml 1 M KCl using the dispenser. Screw the cap onto the tube and shake for 30 minutes. Centrifuge for 15 minutes at 3000 rpm. Decant the supernatant over a filter into a 200 ml volumetric flask. Repeat the shaking and centrifugation step another four times. Decant every time into the same volumetric flask. After the last extraction, wash the filter two times with about 10 ml KCl and fill the flask to the mark with the 1 M KCl solution. Homogenize.

Measurement

Titration of total acidity

Calibrate the pH-meter according to manufacturer's instructions, using buffers of pH = 4 and 7. Pipette 50 ml of the extract into a 100 ml beaker. Place the electrode into the solution and stir magnetically. Titrate with 0.01 M NaOH to endpoint pH=7.8. Check calibration of the pH meter regularly.

Measurement of exchangeable Al

Use the A.A.S. for measurement. For Al the wavelength is 309.3 nm and the flame is a nitrous oxide/acetylene flame. Al can be measured directly in the extract.

Calculation

Total exchangeable acidity

$$Total\ exch.\ acidity\ (cmol(+)\ kg^{-1}\ soil) = \frac{(V-B) \times 4 \times mcf}{W}$$

where

V   = ml NaOH used for sample
B   = ml NaOH used for blank
mcf = moisture correction factor
W   = sample weight (g)
4   = conversion factor

Exchangeable Al

$$Exch.\ Al\ (cmol(+)\ kg^{-1}\ soil) = \frac{(C-Z) \times D \times 2.22 \times mcf}{W}$$

where

C   = Al concentration in sample (mg L^{-1})
Z   = Al concentration in blank (mg L^{-1})
D   = dilution factor (standard = 1, when the sample is not diluted)
mcf = moisture correction factor
W   = sample weight (g)
2.22 = conversion factor

Exchangeable H:

$$Exch.\ H\ (cmol(+)\ kg^{-1}\ soil) = total\ exch.\ acidity - exch.\ Al$$

where

Total exchangeable acidity and exchangeable Al are in cmol(+) kg^{-1} soil

Remarks

- This analysis is only executed when $pH_{KCl} \leq 4.5$.

- Instead of a burette with a pH-meter also an automatic titrator may be used. The end-point should be the same.

- Instead of a pH meter also a 0.1 % phenolphthalein indicator solution may be used to detect the end-point. For this purpose dissolve 100 mg phenolphthalein in 100 ml ethanol 96%.

- Instead of an A.A.S. also an auto analyzer may be used. **(see Velthorst, Section B)**

References

- Begheijn, L.Th., 1980. Methods of Chemical Analyses for Soils and Waters. Dept. of Soil Science and Geology, Agricultural University Wageningen, 3rd ed., page 53-54 .

- Thomas, G.W., 1982. Exchangeable Cations. in: Methods of Soil Analysis. Part 2 - Chemical and Microbiological Properties. Agronomy No. 9 2nd ed., page 159-165.

- Van Lagen, B., 1993. Titration of KCl-extracts for acidity analysis. Intern verslag no 57. Department of Soil Science and Geology, Agricultural University, Wageningen.

A13. KCl-EXTRACTABLE AMMONIUM and NITRATE

Principle

The sample is extracted with a 1M KCl solution. The extracted ammonium is measured colorimetrically as an emerald green complex of ammonium with sodium salicylate, sodium nitroprusside and sodium hypochlorite, using an auto analyzer. After reduction of the extracted nitrate in a copper-cadmium column at pH=7.5 the formed nitrite is measured colorimetrically, using an auto analyzer, as a reddish-purple complex of nitrite, sulphanilamide and N-(1-Naphthyl)ethylene diamine dihydrochloride.

Apparatus

Centrifuge tube with screw cap (50 ml)
Centrifuge
Dispenser for 25 ml
Auto analyzer for ammonium
Auto analyzer for nitrate

Reagents

Potassium chloride (KCl)
Sodium hydroxide 32% (NaOH), special grade for ammonium determination
Sodium potassium tartrate ($NaKC_4H_4O_6.4H_2O$)
Sodium phosphate, dibasic ($Na_2HPO_4.2H_2O$)
Sodium salicylate ($NaC_7H_5O_3$)
Sodium nitroprusside ($Na_2Fe(CN)_5NO.2H_2O$)
Sodium hypochlorite (NaOCl)
Hydrochloric acid 37% (HCl)
Copper (II) sulphate ($CuSO_4.5H_2O$)
Cadmium granules (0.3 - 0.8 mm)
Ammonium chloride (NH_4Cl)
Ammonium hydroxide 25% (NH_4OH)
N-(1-naphthyl)ethylene diamine dihydrochloride ($C_{12}H_{14}N_2.2HCl$)
Sulphanilamide ($C_6H_8N_2O_2 S$)
Brij-35 wetting agent
Sodium nitrate ($NaNO_3$)
Ammonium sulphate (($NH_4)_2SO_4$)

1 M potassium chloride

Dissolve 74.6 g of KCl in 1 litre demineralized water.

20% sodium hydroxide stock solution

Carefully add 625 ml NaOH 32% to 350 ml water. Allow to cool and make up to 1 litre with water. Homogenize.

20% sodium potassium tartrate stock solution

Dissolve 200 g sodium potassium tartrate in 1 litre water. Homogenize.

stock buffer-solution

Dissolve 89 g Sodium phosphate, dibasic in 800 ml hot water. Allow to cool. Add 50 ml 32% NaOH-solution. Allow to cool. Make up to 1 litre with water and homogenize.

working buffer solution

Combine 200 ml stock buffer solution and 250 ml Na,K-tartrate stock solution. Swirl. Add 60 ml 20% NaOH stock solution. Swirl and allow to cool. Make up to 1 litre with water, add 1 ml Brij-35 and homogenize.

sodium salicylate/sodium nitroprusside solution

Dissolve 150 g sodium salicylate and 300 mg sodium nitroprusside in 800 ml water. Make up to 1 litre with water and homogenize. Filter through a folded filter and add 1 ml Brij-35. Mix. **Store in a dark bottle.**

sodium hypochlorite

Add 5.0 ml sodium hypochlorite to 80 ml water. Make up to 100 ml with water and add 2 drops of Brij-35. Homogenize. **Prepare fresh daily.**

2 M hydrochloric acid

Add 160 ml HCl 37% to 800 ml water. Allow to cool and make up to 1 litre with water. Homogenize.

2% copper (II) sulphate solution

Dissolve 2 gram of copper (II) sulphate in 100 ml of water.

ammonium chloride buffer solution

Dissolve 25 g ammonium chloride in about 800 ml water. Add 3 ml ammonium hydroxide 25% and make up to 1 litre with water. Homogenize, add 0.5 ml Brij-35 wetting agent and mix again.

sulphanilamide solution

Add 50 ml HCl 37% to about 600 ml water and mix. Add 5.0 g sulphanilamide and let it dissolve. Make up to 1 litre with water. Homogenize and add 0.5 ml Brij-35 wetting agent and mix again. **Keep this solution in a dark flask!**

N.E.D. solution

Dissolve 0.5 g of N-(1-naphthyl)ethylene diamine dihydrochloride (N.E.D.) in about 800 ml water. Make up to 1 litre with water. Homogenize and add 0.5 ml Brij-35 wetting agent and mix. **Keep this solution in a dark flask!**

1.000 gram nitrate per litre stock solution

Weigh 1.3707 g sodium nitrate (dried at 105° C) in a 400 ml beaker. Dissolve it in about 300 ml water. Transfer the solution to a 1 litre volumetric flask. Make up to volume with water and homogenize.

1.000 gram ammonium per litre stock-solution

Weigh 3.6667 g ammonium sulphate (dried at 105° C.) into a 1 l beaker and dissolve it in about 800 ml water. Transfer it to a 1 litre volumetric flask. Add 1 drop of HCl 37%. Make up to volume with water and homogenize.

2 M potassium chloride

Dissolve 149.2 g of KCl in 1 litre water.

Standard series

Pipette 5 ml of the 1 g L^{-1} ammonium stock solution into a 100 ml volumetric flask. Make up to volume with water and homogenize. This solution is now 50 mg l^{-1} ammonium.

Pipette respectively 0, 2, 4, 6, 8 and 10 ml of both the 1 g L^{-1} nitrate stock solution and the 50 mg L^{-1} ammonium solution into 100 ml volumetric flasks (the same volume of NO_3 and NH_4 to the same flask). Add 50 ml of the 2 M KCl solution to each flask. Make up to volume with water and homogenize. The standard series is now:
Standard 1:   0.0 mg L^{-1} NO_3 and 0.0 mg L^{-1} NH_4
Standard 2:   20.0 mg L^{-1} NO_3 and 1.0 mg L^{-1} NH_4
Standard 3:   40.0 mg L^{-1} NO_3 and 2.0 mg L^{-1} NH_4
Standard 4:   60.0 mg L^{-1} NO_3 and 3.0 mg L^{-1} NH_4
Standard 5:   80.0 mg L^{-1} NO_3 and 4.0 mg L^{-1} NH_4
Standard 6: 100.0 mg L^{-1} NO_3 and 5.0 mg L^{-1} NH_4
(1 mg L^{-1} = 1 ppm)

Procedure

Extraction

Weigh 5 g of soil (accuracy of 1 mg) into a 50 ml centrifuge tube with screw cap. Add 25 ml of the 1 M KCl solution using the dispenser and close the tube. Shake for 2 hours. Centrifuge for 10 minutes at 3500 rpm.

Preparation of the cadmium reduction column

Weigh 3 to 4 gram of cadmium granules in a 100 ml beaker. Wash the granules 3 times with 2 M HCl. Wash thoroughly with distilled water (at least 15 times). Add 50 ml 2% Copper sulphate solution. Mix and allow to stand for 30 minutes. Decant the solution and again wash thoroughly with distilled water (at least 15 times).

Fill the U-formed glass column of the nitrate cartridge with ammonium chloride buffer. Clamp the column in a stand. Add the copper-coated cadmium granules to the column. Fill the column with the granules till both sides are filled to about 5 mm from the top. Prevent air enclosure in the column. Close both ends with quartz wool pre-wetted in ammonium buffer and place it in the nitrate-cartridge of the auto analyzer.

Measurement

Prepare the auto analyzer for measurement following manufacturer's instructions (for flow scheme see Figure 3 and 4). Wavelength for ammonium is 660 nm, flowcell is 5 cm. For nitrate, the wavelength is 520 nm and the flowcell 1.5 cm. Fill the autosampler with standards and samples. Run automatically at a speed of 30 samples per hour. Calculate concentrations of the samples with standards. Run blanks regularly to check the baseline. If the sample is out of the calibration range dilute it with 1 M KCl.

Calculation

$$\text{extractable ammonium, nitrate (mg kg}^{-1}) = \frac{(C-B) \times D \times (25 + (W - (\frac{W}{mcf}))) \times mcf}{W}$$

where

C	= concentration ammonium or nitrate for sample (mg L^{-1})
B	= concentration ammonium or nitrate for blank (mg L^{-1})
D	= dilution factor
W	= sample weight (g)
mcf	= moisture correction factor
25	= volume extractant

Remarks

-   Use distilled water throughout this procedure.

-   When adding the water to the acid, be very careful!!

-   Take care of the sodium hydroxide, because it is very etching.

-   Take special grade 32% NaOH-solution for ammonium determination.

-   Sodium nitroprusside and the cadmium granules are both very toxic. Prevent contact with the skin or the inhalation of cadmium dust.

-   Keep sodium hypochlorite in a refrigerator.

-   Replace the dialyser membrane of the nitrate cartridge every 3 months.

References

-   Van Lagen, B., Manual for Chemical Soil Analyses. Department of Soil Science and Geology, Agricultural University, Wageningen.

-   Velthorst, E.J., 1993. Manual for Chemical Water Analyses. Department of Soil Science and Geology, Agricultural University, Wageningen.

Figure 3. Flow scheme for ammonium determination

AMMONIUM

to sampler wash receptacle
grn/grn (2.00) water
blk/blk (0.32) air
gry/gry (1.00) working buffer solution
orn/grn (0.10) sample
blk/blk (0.32) Na-salicylate/Na-nitroprusside solution
orn/yel (0.16) Na-hypochlorite solution
yel/yel (1.20) from flow cell
flow rates in ml/min

waste

37°C
7.7 ml

waste
to flow cell

colorimeter
flow cell: 50 mm
filter : 660 nm
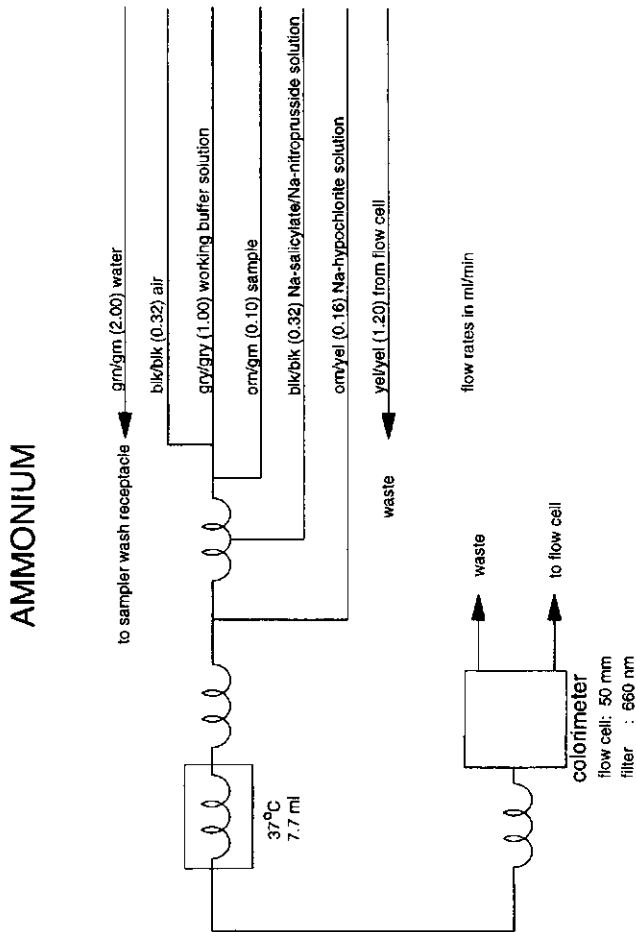
Figure 4. Flow scheme for nitrate determination
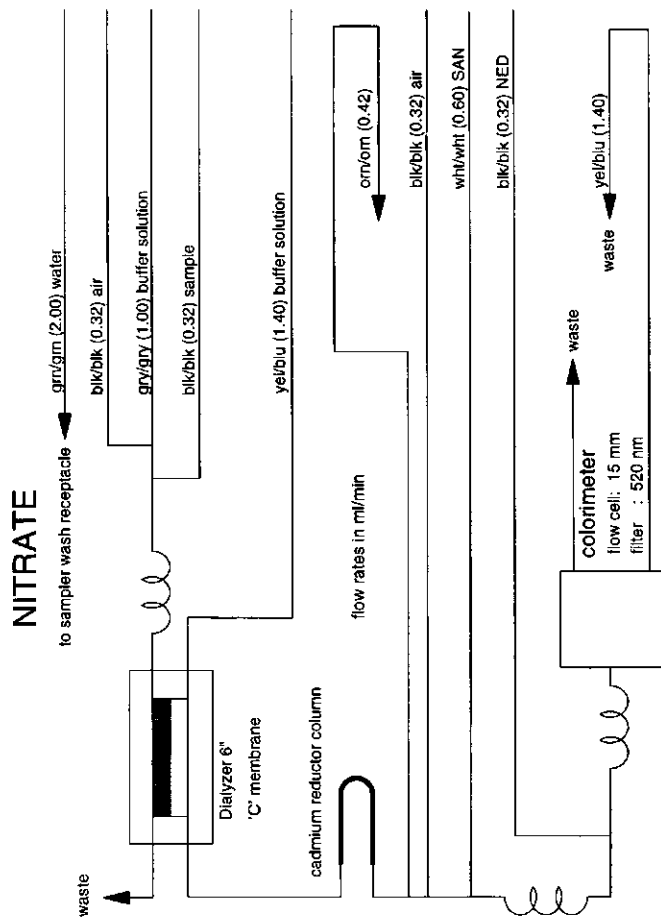
A14: "FREE" Fe and Al

Principle

The "free" iron and aluminium compounds, as goethite and gibbsite, are extracted after reduction of Fe with dithionite in a buffer of citrate and dithionite. This method is called the "Holmgren"-method. In some cases also manganese and/or silica are measured in this extract. The elements are measured with atomic absorption spectrometry (A.A.S.).

Apparatus

Shaking machine
Dispenser for 100 ml
Centrifuge
Diluter
A.A.S. with a nitrous oxide burner

Reagents

Sodium citrate ($Na_3(C_6H_5O_7).2H_2O$)
Sodium dithionite ($Na_2S_2O_4$)
"Superfloc" (flocculation agent)
Ampoules for 1000 mg L^{-1} Fe and Al (if necessary also for Mn and Si)

17% citrate/1.7% dithionite extractant

Dissolve 170 g sodium citrate and 17 g sodium dithionite in 1 distilled litre water. **This solution must be made freshly every day.**

0.2% "Superfloc"

Dissolve 100 mg superfloc in 50 ml water by stirring it overnight in the dark. This solution can be kept for about a week when stored in the dark

1000 mg L^{-1} standard solutions for Fe, Al, Mn and Si

Dilute the respective ampoules according to the manufacturer's instructions.

Standard series

Fe and Al

Pipette 10 ml of the 1000 mg L^{-1} Fe stock solution and 20 ml of the 1000 mg L^{-1} Al stock solution into a 100 ml volumetric flask. Make up to volume with water and homogenize. This combined standard solution is now 100 mg L^{-1} Fe and 200 mg L^{-1} Al.

Pipette 0, 5, 15 and 25 ml of the combined standard solution into 100 ml volumetric flasks. Add 20 ml of the extractant to each flask. Fill each flask to the mark with water and homogenize. The combined standard series is now:

Standard 1:   0.0 mg L^{-1} Fe and 0.0 mg L^{-1} Al
Standard 2:   5.0 mg L^{-1} Fe and 10.0 mg L^{-1} Al
Standard 3: 15.0 mg L^{-1} Fe and 30.0 mg L^{-1} Al
Standard 4: 25.0 mg L^{-1} Fe and 50.0 mg L^{-1} Al

Mn

Pipette 10 ml of the 1000 mg L^{-1} Mn stock solution into a 250 ml volumetric flask. Make to volume with water and homogenize. This standard solution is now 40 mg L^{-1} Mn.

Pipette 0, 5, 15 and 25 ml of the standard solution into 100 ml volumetric flasks. Add 20 ml of the extractant to each flask. Fill each flask to the mark with water and homogenize. The standard series is now:

Standard 1:   0.0 mg L^{-1} Mn
Standard 2:   2.0 mg L^{-1} Mn
Standard 3:   6.0 mg L^{-1} Mn
Standard 4: 10.0 mg L^{-1} Mn

Si

Pipette 20 ml of the 1000 mg L^{-1} Si stock solution into 100 ml volumetric flasks. Make to volume with water and homogenize. This standard solution is now 200 mg L^{-1} Si.

Pipette 0, 5, 15 and 25 ml of the standard solution into a 100 ml volumetric flask. Add 20 ml of the extractant to each flask. Fill each flask to the mark with water and homogenize. The standard series is now:

Standard 1:   0.0 mg L^{-1} Si
Standard 2: 10.0 mg L^{-1} Si
Standard 3: 30.0 mg L^{-1} Si
Standard 4: 50.0 mg L^{-1} Si

Errata for: Manual for Soil and Water Analysis; P. Buurman, B. van Lagen & E.J. Velthorst (eds) (1996).

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Calculation for dithionite-extractable Fe, Al, Mn and Si

$$\text{"Free" Fe, Al, Mn or Si (\%)} = \frac{(C-B) \times D \times (60 + (W - \frac{W}{mcf}))) \times mcf}{W \times 10000}$$

where

C = concentration Fe, Al, Mn or Si in sample (mg L⁻¹)

B = concentration Fe, Al, Mn or Si in blank (mg L⁻¹)

D = dilution factor (standard 5 for Al, Si and Mn; 50 for Fe)

mcf = moisture correction factor

W = sample weight (g)

60 = volume of extractant (ml)

10000 = conversion factor

Calculation for ammonium oxalate-extractable Fe, Al and Si

$$\text{"amorphous" Fe, Al or Si (\%)} = \frac{(C-B) \times D \times (50 + (W - (\frac{W}{mcf}))) \times mcf}{W \times 10000}$$

where

C = concentration Fe, Al or Si in sample (mg L⁻¹)

B = concentration Fe, Al or Si in blank (mg L⁻¹)

D = dilution factor (standard is 5 or 20)

mcf = moisture correction factor

W = sample weight (g)

50 = volume of extractant (ml)

10000 = conversion factor

Procedure

extraction

Weigh about 1000 mg (accuracy 1 mg) of sample into a 100 ml shaking bottle. Add 60.0 ml extractant using a dispenser. Shake overnight. Transfer at least 25 ml of the extract to a 50 ml centrifuge tube and add 3 drops of the superfloc solution. Shake vigorously and centrifuge for 15 minutes at 2500 rpm. Keep the supernatant for measurement of Fe, Al, Mn and Si.

dilution

The supernatant is diluted 5 times for Al, Si and Mn and 50 times for Fe. To make the measurement faster and better, the dilutions are made with the same background.
5 times dilution: Dilute the supernatant 1+4 times with water.
50 times dilution: Dilute the supernatant 1+9 times with the extractant. Dilute this diluted extractant 1+4 times with water.

Measurement

Use the A.A.S. for measurement. For the important settings see Table 2.

Table 2 Settings for measurement of the citrate/dithionite extracted elements

element	Wavelength (nm)	gas mixture
Fe	248.3	air/acetylene
Al	309.3	nitrous oxide/acetylene
Mn	279.5	nitrous oxide/acetylene
Si	251.6	nitrous oxide/acetylene

Calculation

$$\text{"Free" Fe, Al, Mn or Si (\%)} = \frac{(C-B) \times D \times (60 + (W - (\frac{W}{mcf}))) \times mcf}{W \times 10}$$

where

C   = concentration Fe, Al, Mn or Si in sample (mg L^{-1})
B   = concentration Fe, Al, Mn or Si in blank (mg L^{-1})
D   = dilution factor (standard 5 for Al, Si and Mn; 50 for Fe)
mcf = moisture correction factor
W   = sample weight (mg)
10   = conversion factor

Sometimes one wants to know the concentration as oxide instead of elements. The conversion for this is:

$$\%Fe_2O_3 = 1.43 \times \%Fe$$
$$\%Al_2O_3 = 1.89 \times \%Al$$
$$\%MnO_2 = 1.58 \times \%Mn$$
$$\%SiO_2 = 2.14 \times \%Si$$

Remarks

-       Superfloc is a flocculant. It should not contain any of the elements that are to be measured and should be chemically and physically inert.

-       When Al and/or Si has to be measured, use distilled water throughout the analyses.

-       Mn may also be measured with an air/acetylene flame, but the results are more accurate when using a nitrous oxide/acetylene flame.

-       When a 50 times dilution is not enough to measure the elements, the analysis should be repeated with less sample.

References

-       Holmgren, G.G.S., 1967. A rapid citrate-dithionite extractable iron procedure. Soil Science Society of America Proceedings 31:210-211.

-       Van Reeuwijk, L.P., 1992. Procedure for Soil Analysis. I.S.R.I.C. Technical Paper 9, 3rd ed., page 12-3 and 12-4.

A15: "AMORPHOUS" Fe, Al and Si

Principle

The "amorphous" iron, aluminium and silica compounds are extracted in an acid oxalate solution. The elements are measured with A.A.S. For calcareous samples this procedure is adapted by Del Campillo and Torrent (1992).

Apparatus

Shaking machine
Dispenser of 50 ml
Centrifuge
Diluter
A.A.S. with nitrous oxide burner

Reagents

Ammonium oxalate (($COONH_4$)$_2$.H_2O)
Oxalic acid (($COOH$)$_2$.$2H_2O$)
"Superfloc" (flocculation agent)
Hydrochloric acid (37%) (HCl)
Potassium chloride (KCl)
Ampoules for 1000 mg L^{-1} Fe, Al and Si

      ammonium oxalate extractant

Dissolve 16.2 g ammonium oxalate and 10.8 g oxalic acid in 1 litre distilled water. Adjust pH to 3 by adding one of the components.

      0.2% "Superfloc"

Dissolve 100 mg superfloc in 50 ml water by stirring it overnight in the dark. This solution can be kept for about a week, when stored in the dark.

      5 x dilution solution

Dissolve 2.38 g KCl in about 800 ml water. Carefully add 25 ml concentrated HCl. Allow to cool and make up to 1 litre with water. Homogenize.

      20 x dilution solution

Dissolve 2.01 g KCl in 600 ml water. Add 210 ml of the extractant and carefully add 21 ml concentrated HCl. Allow to cool and make up to 1 litre with water. Homogenize.

1000 mg L^{-1} standard solutions for Fe, Al and Si

Dilute the respective ampoules according to the manufacturer's instructions.

10000 mg L^{-1} K suppressant solution

Dissolve 19 g KCl in about 800 ml water and make up to 1 litre with water.

Standard series

Fe and Al

Pipette 10 ml of the 1000 mg L^{-1} Fe stock solution and 20 ml of the 1000 mg L^{-1} Al stock solution to a 100 ml volumetric flask. Make up to volume with water and homogenize. This combined standard solution is now 100 mg.L^{-1} Fe and 200 mg.L^{-1} Al.
Pipette 0, 5, 15 and 25 ml of the combined standard solution into 100 ml volumetric flasks. Add 10 ml of the extractant, 5 ml of the K suppressant solution and 1 ml concentrated HCl to each flask. Fill each flask to the mark with water and homogenize. The combined standard series is now:
Standard 1:   0.0 mg L^{-1} Fe and 0.0 mg L^{-1} Al
Standard 2:   5.0 mg L^{-1} Fe and 10.0 mg L^{-1} Al
Standard 3: 15.0 mg L^{-1} Fe and 30.0 mg L^{-1} Al
Standard 4: 25.0 mg L^{-1} Fe and 50.0 mg L^{-1} Al

Si

Pipette 20 ml of the 1000 mg L^{-1} Si stock solution to a 100 ml volumetric flask. Make up to volume with water and homogenize. This standard solution is 200mg.L^{-1} Si.
Pipette 0, 5, 15 and 25 ml of the standard solution to 100 ml volumetric flasks. Add 10 ml of the extractant, 5 ml of the K suppressant solution and 1 ml concentrated HCl to each flask. Fill each flask to the mark with water and homogenize. The standard series is now:
Standard 1:   0.0 mg L^{-1} Si
Standard 2: 10.0 mg L^{-1} Si
Standard 3: 30.0 mg L^{-1} Si
Standard 4: 50.0 mg L^{-1} Si

Procedure

extraction

Weigh about 1000 mg (accuracy 1 mg) of sample into a 100 ml shaking bottle. Add 50 ml extractant using a dispenser. Shake for 4 hours in the dark. Transfer at least 25 ml of extract to a 50 ml centrifuge tube and add 3 drops of the superfloc solution. Shake vigorously and centrifuge for 15 minutes at 2500 rpm. Keep the

supernatant for measurement of Fe, Al and Si.

dilution:

The supernatant is diluted 5 and 20 times. To make the measurement faster and better 2 dilutions are made with the same matrix.
5 times dilution: dilute the supernatant 1+4 with the 5 x dilution solution.
20 times dilution: dilute the supernatant 1+19 times with the 20 x dilution solution.

Measurement

Use the A.A.S. for measurement (See Table 3).

Table 3 Settings for measurement of the oxalate extracted elements

element	Wavelength (nm)	gas mixture
Fe	248.3	air/acetylene
Al	309.3	nitrous oxide/acetylene
Si	251.6	nitrous oxide/acetylene

Calculation

$$\text{"amorphous" Fe, Al or Si (\%)} = \frac{(C-B) \times D \times (50 + (W - (\frac{W}{mcf}))) \times mcf}{W \times 10}$$

where

C = concentration Fe, Al or Si in sample (mg L^{-1})
B = concentration Fe, Al or Si in blank (mg L^{-1})
D = dilution factor (standard is 5 or 20)
mcf = moisture correction factor
W = sample weight (mg)
50 = volume extractant

Sometimes one wants to know the concentration as oxide instead of elements. The conversion for this is:

$$%Fe_2O_3 = 1.43 \times %Fe$$
$$%Al_2O_3 = 1.89 \times %Al$$
$$%SiO_2 = 2.14 \times %Si$$

Remarks

- Superfloc is a coagulant. It should not contain any of the elements that are to be measured and should be chemically and physically inert.

- When Al and/or Si has to be measured, use distilled water throughout the analyses.

- When a 20 times dilution is not enough to measure the elements, the analysis should be repeated with less sample. It is also possible to extract 1000 mg of sample in 100 ml extractant in a 250 ml shaking bottle. The conversion factor in the calculation is then 10 instead of 5.

References

- Del Campillo, M.C. and J. Torrent, 1992. A rapid acid-oxalate extraction procedure for the determination of active Fe-oxide forms in calcareous soils. Zeitschrift für Pflanzenernährung und Bodenkunde, 155 (5/6): 437-440.

- Van Reeuwijk, L.P., 1992. Procedure for Soil Analysis. I.S.R.I.C. Technical Paper 9, 3rd ed., page 12-5 and 12-6.

A16: PYROPHOSPHATE EXTRACTABLE Fe, Al and C.

Principle

The Fe and Al bound to organic matter in the soil is extracted at a high pH (>9) in a sodium pyrophosphate solution. Fe and Al are measured with A.A.S. The dissolved carbon is measured with the elemental analyzer, after drying the extract.

Apparatus

Shaking machine
Dispenser for 100 ml
Centrifuge
Diluter
A.A.S. with a nitrous oxide burner
Hot plate
Aluminium reaction plate
Stannum liquid-phase cup
Soxhlet set-up
Micro-pipette for 50 µl
Elemental analyzer.

Reagents

Sodium pyrophosphate (=sodium diphosphate) ($Na_4P_2O_7.10H_2O$)
"Superfloc" (flocculating agent)
Ampoules for 1000 mg L^{-1} Fe and Al
Hexane
Acetone
Potassium hydrogen phthalate ($C_8H_5O_6K$)
UHQ-water
Magnesium perchlorate anhydrous ($Mg(ClO_4)_2$)

> 0.1 M sodium pyrophosphate extractant

Dissolve 44.6 g $Na_4P_2O_7.10H_2O$ in 1 litre water.

> 0.2% "Superfloc"

Dissolve 100 mg superfloc in 50 ml water by stirring it overnight in the dark. This solution can be kept for about a week, when stored in the dark.

1000 mg L^{-1} standard solutions for Fe and Al

Dilute the respective ampoules according to the manufacturer's instructions.

1000 mg L^{-1} standard solution for dissolved carbon

Weigh in 1063.7 mg potassium hydrogen phthalate in a 250 ml beaker. Add 200 ml UHQ-water and allow the phthalate to dissolve. Transfer the solution to a 500 ml volumetric flask. Make up to volume with UHQ-water and homogenize. This solution is also the highest standard for the carbon measurement.

Standard series

Fe and Al

Pipette 10 ml of the 1000 mg L^{-1} Fe stock solution and 20 ml of the 1000 mg L^{-1} Al stock solution to a 100 ml volumetric flask. Make up to volume with water and homogenize. This combined standard solution is now 100 mg L^{-1} Fe and 200 mg L^{-1} Al.

Pipette 0, 5, 15 and 25 ml of the combined standard solution to 100 ml volumetric flasks. Add 20 ml of the extractant to each flask. Fill each flask to the mark with water and homogenize. The combined standard series is now:

Standard 1: 0.0 mg L^{-1} Fe and   0.0 mg L^{-1} Al
Standard 2: 5.0 mg L^{-1} Fe and 10.0 mg L^{-1} Al
Standard 3: 15.0 mg L^{-1} Fe and 30.0 mg L^{-1} Al
Standard 4: 25.0 mg L^{-1} Fe and 50.0 mg L^{-1} Al

Dissolved carbon

Pipette respectively 0, 2.5, 5, 10, 15 and 20 ml of the 1000 mg L^{-1} C to 25 ml volumetric flasks. Make up to volume with UHQ-water and homogenize. The standard series is now:

Standard 1:   0 mg L^{-1} C
Standard 2:   100 mg L^{-1} C
Standard 3:   200 mg L^{-1} C
Standard 4:   400 mg L^{-1} C
Standard 5:   600 mg L^{-1} C
Standard 6:   800 mg L^{-1} C
Standard 7: 1000 mg L^{-1} C

Procedure

extraction

Weigh about 1000 mg (accuracy 1 mg) of sample into a 250 ml shaking bottle. Add 100 ml extractant, using a dispenser. Shake overnight. Transfer at least 25 ml of

extractant to a 50 ml centrifuge tube and add 3 drops of the superfloc solution. Shake vigorously and centrifuge for 15 minutes at 2500 rpm (see remark). Keep the supernatant for measurement of Fe en Al.

For carbon analysis bring about 10 ml of extract to a 15 ml centrifuge tube and centrifuge for at least 30 min at 4000 rpm. **Don't add superfloc!**

dilution for Fe and Al measurement:

5 times dilution: Dilute the supernatant 1+4 with water. If this dilution is not enough then it is possible to dilute the diluted extract 1+1 with the blank of the standard series. If this is not enough either, make a suitable dilution, but make sure that the background has the same concentration of sodium pyrophosphate (0.02 M) as the standard series.

Measurement

Fe and Al

Use the A.A.S. for measurement. For Fe the wavelength is 248.3 nm and the flame is an air/acetylene flame. For Al the wavelength is 309.3 nm and the flame is a nitrous oxide/acetylene flame.

dissolved carbon

Cleaning of the stannum cups for solutions:
Clean the cups by a soxhlet extraction with a 1:1 hexane:acetone mixture for 8 hours. Dry them overnight at 250° C. Keep them in a dessicator.

sample preparation:
Pipette 50 μl of each standard or the sample in a separate stannum cup. Place it in the aluminium block and heat till a temperature of 65° C. Let it dry for at least 1 hour. If the sample is supposed to contain less carbon then the 100 mg carbon per litre standard, pipette another volume of 50 μl of sample to the cup and dry again. The blanks of the series need to be pipetted the same number of volumes as the sample.

Measurement

Measure carbon according to the manufacturer's instructions using the instrumental settings of Table 3. The formed water is trapped by a column filled with $Mg(ClO_4)_2$.

Table 3: Instrumental setting for the pyrophosphate extractable carbon measurement by elemental analyser

Parameter	setting	Parameter	setting
Oven temperature of oxidation column	980° C	Sampler closed after	15 seconds
Oven temperature of reduction column	650° C	Oxygen injection during	40 seconds
Oven temperature of gaschromatograph	60° C	Peak enabling	30 seconds
Filament temperature	190° C	Helium flow	±90 ml min^{-1}
Cycle time	260 seconds	Purge flow	40 ml min^{-1}
Sampler open after	10 seconds	Oxygen flow	20 ml min^{-1}

The integration of the formed carbon peak is done by the managment software of the system. This software gives the value for the peak area of the peak. The regression of the peak areas of the standards is calculated. The carbon concentration is calculated from the regression curve.

Calculation

$$\text{"organic" Fe or Al (\%)} = \frac{(C-B) \times D \times (100 + (W - (\frac{W}{mcf}))) \times mcf}{W \times 10}$$

where

C = concentration Fe or Al in sample (mg L^{-1})
B = concentration Fe or Al in blank (mg L^{-1})
D = dilution factor
mcf = moisture correction factor
W = sample weight (mg)
100 = volume extractant

Sometimes one wants to know the concentration as oxide in stead of elements. The conversion for this is:

$$\%Fe_2O_3 = 1.43 \times \%Fe$$
$$\%Al_2O_3 = 1.89 \times \%Al$$

$$\text{dissolved organic carbon (\%)} = \frac{(C-B) \times (100 + (W - (\frac{W}{mcf}) \times mcf}{W \times n \times 10}$$

where

C   = concentration C in sample (mg L^{-1})
B   = concentration C in blank (mg L^{-1})
n   = number of pipetted 50 µl volumes
mcf = moisture correction factor
W   = sample weight (mg)
100 = volume extractant

Remarks

- Superfloc is an organic coagulant. It should not contain any of the elements to be measured and should be chemically and physically inert. For the carbon measurement the material should **not** be used for obtaining a clear solution!!

- Because pyrophosphate is also a dispersing agent, it is very difficult to get a clear supernatant. Check if supernatant is clear by taking a part of the extract in pasteur pipet. If the extract is not clear, repeat the centrifugation after the addition and mixing of some extra "superfloc" or use a superspeed unit in the centrifuge.

References

- Van Lagen, B., 1996. Measuring Dissolved Organic Carbon in Pyrophosphate Extracts by Elemental Analyzer. (submitted for publication).

- Van Reeuwijk, L.P., 1992. Procedure for Soil Analysis. I.S.R.I.C. Technical Paper 9, 3rd ed., page 12-7 and 12-8.

"AVAILABLE" PHOSPHORUS.

Two procedures for analyzing "available" phosphorus are described here, the "Bray I" method for acid soils and the "Olsen" method for other soils.

A17: P-BRAY I

Principle

Phosphate is extracted in an acid ammonium fluoride solution. After the extraction, the phosphate is determined colorimetrically with ammonium molybdate as the colouring reagent. This method is used for acidic soils.

Apparatus

Dispenser for 25 ml
Spectrophotometer

Reagents

Ammonium fluoride (NH_4F)
Hydrochloric acid 37% (HCl)
Boric acid (H_3BO_3)
Sulphuric acid 96% (H_2SO_4)
Ammonium molybdate (($NH_4)_6Mo_7O_{24}.4H_2O$)
Potassium antimony-(III) oxide tartrate ($K(SbO)C_4H_4O_6.\frac{1}{2}H_2O$)
(L+)-Ascorbic acid ($C_6H_8O_6$)
Ampoule for 1000 mg L^{-1} P or potassium dihydrogen phosphate (KH_2PO_4)

     1 M ammonium fluoride

Dissolve 3.7 g NH_4F in 100 ml distilled water. Store it in a polythene bottle.

     0.5 M hydrochloric acid

Bring 80 ml water to a 100 ml measuring cylinder. Add 4.3 ml HCl 37%. Allow to cool and make to 100 ml with water. Homogenize.

     Extractant

Bring 460 ml water to 500 ml measuring cylinder. Add 15 ml of the 1 M NH_4F solution and 25 ml of the 0.5 M HCl solution. Homogenize. Store it in a polythene bottle.

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1% boric acid solution

Dissolve 1 g H_3BO_3 in 100 ml water.

2.5 M sulphuric acid

Carefully add 35 ml H_2SO_4 96% to 200 ml water. Allow to cool and make to 250 ml with water. Homogenize.

4% ammonium molybdate

Dissolve 4 g $(NH_4)_6Mo_7O_{24}.4H_2O$ in 100 ml water. Store it in a polythene bottle in the dark.

0.275% potassium antimony-(III) oxide tartrate

Dissolve 275 mg $K(SbO)C_4H_4O_6.\frac{1}{2}H_2O$ in 100 ml water.

1.75% ascorbic acid

Dissolve 1.75 g ascorbic acid in 100 ml water. **Prepare fresh daily.**

Mixed reagent

Add, using a measuring cylinder, successively the following reagents to a 500 ml bottle:
-    50   ml 2.5 M H_2SO_4
-    15   ml 4% ammonium molybdate
-    30   ml 1.75% ascorbic acid
-     5   ml 0.275% potassium antimony-(III) oxide tartrate
-   200   ml water
Mix well after each addition and prepare fresh daily.

1000 mg L^{-1} P stock-solution

Dilute the ampoule according to manufacturer's instructions. Alternatively, weigh 4.3943 g KH_2PO_4 (dried at 105°C) into a 250 ml beaker. Add about 200 ml of water and let the KH_2PO_4 dissolve. Transfer the solution to a 1 litre volumetric flask. Make up to volume and homogenize.

Standard series

Pipette 10 ml of the 1000 mg L^{-1} stock solution in a 100 ml volumetric flask. Make up to volume with water and homogenize. This makes a 100 mg L^{-1} P solution.
Pipette 30 ml of this 100 mg L^{-1} P solution to a 250 ml volumetric flask. Make to volume with water and homogenize. This makes a 12 mg L^{-1} P solution.
Pipette of this 12 mg L^{-1} P solution respectively 0, 5, 10, 15, 20 and 25 ml to a 50 ml volumetric flask. Make each flask to volume with water and homogenize. The standard series is then: standard 1: 0.0 mg L^{-1} P
                      standard 2: 1.2 mg L^{-1} P
                      standard 3: 2.4 mg L^{-1} P
                      standard 4: 3.6 mg L^{-1} P
                      standard 5: 4.8 mg L^{-1} P
                      standard 6: 6.0 mg L^{-1} P

Procedure

Weigh 2 g (accuracy 0.01 g) of sample into a 50 ml shaking bottle. Add, using the dispenser, 14.0 ml of the extractant. Shake for 1 minute by hand. Immediately, filter over a hardened filter (e.g. Whatman 42). If the filtrate is turbid, filter again over the same filter. The filtration may not exceed 10 minutes.
Pipette successively in a test tube: - 1 ml of the standard series, sample or blank,
                                            - 2 ml boric acid solution and
                                            - 3 ml mixed reagent.
Homogenize and allow to stand for at least 1 hour for the blue colour to reach its maximum.

Measurement

Measure the absorbance of the solution at 882 or 720 nm, using the spectrophotometer. If the sample is out of the calibration range, dilute the extract with water and measure this diluted extract as described above. Measure also the standards again.

Calculation

Prepare a plot of P-concentration against absorbance. Read or calculate the P concentration of the sample from this plot.

$$\text{"available" } P \text{ (mg kg}^{-1}) = \frac{(C-B) \times D \times (14 + (W - (\frac{W}{mcf}))) \times mcf}{W}$$

where

C   = P concentration in sample (mg L^{-1})
B   = P concentration in blank (mg L^{-1})
D   = dilution factor (standard 1 for undiluted samples)
mcf = moisture correction factor
W   = sample weight (g)
14   = volume extractant

Remarks

-      Because the mixed reagent also may colour Si-compounds, all reagents and materials must be Si-free.

- Because demineralized water may contain silica, distilled water has to be used for this analysis.

- Because the phosphate/molybdate complex has two different optima in its spectrum, it may be measured at 882 and 720 nm.

References

- Olsen, S.R. and L.E. Sommers, 1982. Phosphorus. in: Methods of Soil Analysis. part 2 - Chemical and Microbiological Properties. Agronomy No.9, 2nd ed., page 403-430.

- Van Reeuwijk, L.P., 1992. Procedures for Soil Analysis. I.S.R.I.C. Technical Paper no. 9, 3rd ed., page 14-1 and 14-2.

A18: P-OLSEN

Principle

The phosphate in the sample is extracted with a sodium bicarbonate solution of pH=8.5. Thereafter, it is determined colorimetrically with ammonium molybdate as colouring reagent. This method is used for alkaline, calcareous or neutral soils.

Apparatus

Dispenser for 100 ml
Shaking machine
Spectrophotometer

Reagents

Sodium hydroxide (NaOH)
Sodium bicarbonate (NaHCO$_3$)
Sulphuric acid 96% (H$_2$SO$_4$)
Ammonium molybdate ((NH$_4$)$_6$Mo$_7$O$_{24}$.4H$_2$O)
Potassium antimony-(III) oxide tartrate (K(SbO)C$_4$H$_4$O$_6$.½H$_2$O)
(L+)-Ascorbic acid (C$_6$H$_8$O$_6$)
Ampoule for 1000 mg L^{-1} P

1 M NaOH

Dissolve 4 g NaOH in 100 ml of distilled water

0.5 M sodium bicarbonate extractant

Dissolve 42 g NaHCO$_3$ in 1 litre water. Adjust the pH to 8.5 with 1 M NaOH. (Check pH every day.)

4 M sulphuric acid

Carefully add 56 ml H$_2$SO$_4$ 96% to 150 ml water. Allow to cool and make to 250 ml with water. Homogenize.

4% ammonium molybdate

Dissolve 4 g (NH$_4$)$_6$Mo$_7$O$_{24}$.4H$_2$O in 100 ml water. **Store it in a polythene bottle in the dark.**

0.275% potassium antimony-(III) oxide tartrate

Dissolve 275 mg K(SbO)C$_4$H$_4$O$_6$.½H$_2$O in 100 ml water.

1.75% ascorbic acid

Dissolve 1.75 g ascorbic acid in 100 ml water. Prepare fresh daily.

Mixed reagent

Using a measuring cylinder, add successively the following reagents to a 500 ml bottle:
- 50 ml   4 M H_2SO_4
- 15 ml   4% ammonium molybdate
- 30 ml   1.75% ascorbic acid
-   5 ml   0.275% potassium antimony-(III) oxide tartrate
-200 ml   water

Mix well after each addition and prepare fresh daily.

1000 mg L^{-1} P stock solution

Dilute the ampoule according to manufacturer's instructions. Alternatively, weigh   4.3943 g KH_2PO_4 (dried at 105° C) into a 250 ml beaker. Add about 200 ml of water and let the KH_2PO_4 dissolve. Bring the solution over to a 1l volumetric flask. Make up to volume and homogenize.

Standard series

Pipette 10 ml of the 1000 mg L^{-1} P stock solution in a 100 ml volumetric flask. Make up to volume with water and homogenize. This makes a 100 mg L^{-1} P solution.
Pipette 10 ml of this 100 mg L^{-1} P solution to a 250 ml volumetric flask. Make to volume with extracting solution and homogenize. This makes a 4 mg L^{-1} P solution.
Pipette of this 4 mg L^{-1} P solution respectively 0, 5, 10, 15, 20 and 25 ml to a 50 ml volumetric flask. Make each flask to volume with extractant and homogenize. The standard series is now:
standard 1: 0.0 mg L^{-1} P
standard 2: 0.4 mg L^{-1} P
standard 3: 0.8 mg L^{-1} P
standard 4: 1.2 mg L^{-1} P
standard 5: 1.6 mg L^{-1} P
standard 6: 2.0 mg L^{-1} P

Procedure

Weigh 5 g (accuracy 0.01 g) of sample into a 250 ml shaking bottle. Add 100 ml sodium bicarbonate extractant by dispensette and shake for 30 minutes. Filter through a hardened filter (e.g. Whatman 42). Pipette 5 ml of the standard series, blank or sample to a test tube (of at least 20 ml). Carefully add (because of carbon dioxide evolution) 5 ml of the mixed reagent. Homogenize and allow to stand for at least 1 hour for the blue colour to reach its maximum.

Measurement

Measure the absorbance of the solution at 882 or 720 nm, using the spectrophotometer. If the sample is out of the calibration-range, dilute the extract with extractant and measure this diluted extract as described above. Measure also the standard range once again.

Calculation

Prepare a plot of P-concentration against absorbance. Read or calculate the P concentration of the sample from this plot.

$$\text{"available" } P \text{ (mg kg}^{-1}) = \frac{(C-B) \times D \times (100 + (W - (\frac{W}{mcf}))) \times mcf}{W}$$

where

C   = P concentration in sample (mg L^{-1})
B   = P concentration in blank (mg L^{-1})
D   = dilution factor
mcf = moisture correction factor
W   = sample weight (g)
100 = conversion factor

Remarks

- Because the mixed reagent also may colour Si-compounds, all reagents and materials must be free of Si.

- Because demineralized water may contain silica, distilled water has to be used for this analysis.

- Because the phosphate/molybdate complex has two different optima in its spectrum, it may be measured at 882 and 720 nm.

References

- Olsen, S.R. and L.E. Sommers, 1982. Phosphorus. in: Methods of Soil Analysis. part 2 - Chemical and Microbiological Properties. Agronomy No.9, 2nd ed., page 403-430.

- Van Reeuwijk, L.P., 1992. Procedures for Soil Analysis. I.S.R.I.C. Technical Paper no. 9, 3rd ed., page 14-3 and 14-4.

A19: PHOSPHATE RETENTION

Principle

The sample is treated with a phosphate solution of pH=4.6. The phosphate remaining in solution, which is not complexed by the soil, is determined colorimetrically with ammonium vanadate as the colouring reagent.

Apparatus

Dispenser for 25 ml
Shaking machine
Centrifuge
Diluter
Spectrophotometer

Reagents

Potassium dihydrogen phosphate (KH_2PO_4)
Sodium acetate, anhydrous (CH_3COONa)
Acetic acid glacial (CH_3COOH)
Ammonium monovanadate (NH_4VO_3)
Ammonium molybdate (($NH_4)_6Mo_7O_{24}.4H_2O$)
Nitric acid 65% (HNO_3)

    1000 mg L^{-1} P retention solution

Dissolve 4.40 g KH_2PO_4 and 16.4 g CH_3COONa in about 800 ml distilled water. Add 11.5 ml acetic acid glacial and transfer it to 1 litre volumetric flask. Make to volume with water and homogenize. The pH should be 4.6±0.1.

    ammonium vanadate solution

Dissolve 0.4 g NH_4VO_3 in about 450 ml boiling water. Allow to cool and add 3 ml concentrated HNO_3. Make to 500 ml with water and homogenize.

    ammonium molybdate solution

Dissolve 8 g $(NH_4)_6Mo_7O_{24}.4H_2O$ in about 400 ml water at a temperature of 50°C. Allow to cool and make to 500 ml with water. Homogenize.

    Mixed reagent

Bring 400 ml water to a 2000 ml beaker. Carefully add 50 ml concentrated HNO_3. Allow to cool and make to 500 ml with water. Homogenize. Add to the diluted HNO_3 first the ammonium vanadate solution and thereafter the ammonium molybdate solution. Homogenize. **Mix well after each addition.**

Standard series

Pipette respectively 0, 10, 20, 30 and 40 ml of the P retention solution (=standard 6) into 50 ml volumetric flasks. Make up to volume with water and homogenize. The standard series is now:
standard 1: 100% P retention
standard 2: 80% P retention
standard 3: 60% P retention
standard 4: 40% P retention
standard 5: 20% P retention
standard 6:   0% P retention

Procedure

Weigh 5 g (± 0.05 g) of sample into a 50 ml shaking bottle. Add 25.0 ml P retention solution with the dispenser and shake overnight (16 hours). Transfer the suspension to a 50 ml centrifuge tube and centrifuge for 10 minutes at 2500 rpm. Dilute the standard series and the sample 20 (e.g. 1+19) times with the mixed reagent. Allow the colour to reach it maximum for at least 30 minutes and measure at 466 nm within 24 hours, using the spectrophotometer.

Calculation

Prepare a plot of P retention against absorbance. Read or calculate the P retention of the sample from this plot and report it in percentage P retention.

Remarks

-       Use distilled water throughout the procedure.

References

-       Blakemore, L.C., P.L. Searle and B.K. Daly, 1987. Methods for Chemical Analysis of Soils. N.Z. Soil Bureau Sci. Rep. 80., Soil Bureau, Lower Hutt, New Zealand, page 44.

-       Van Reeuwijk, L.P., 1992. Procedures for Soil Analysis. I.S.R.I.C. Technical Paper no. 9, 3rd ed., page 14-7.

A20: WATER-SOLUBLE SALTS

Principle

Water soluble salts in the soil are dissolved in a 1:5 (soil:water) or a saturated extract. The pH is measured potentiometrically, carbonate and bicarbonate are measured titrimetrically. The cations are measured with A.A.S./A.E.S. and the anions are measured with high performance liquid chromatography (H.P.L.C.). For the saturation extract, the moisture content is determined.

Apparatus

Dispenser for 100 ml
Shaking machine
Büchner funnel
Drying oven
pH meter with combined electrode
Conductivity meter with conductivity cell
Magnetic stirrer
Diluter
A.A.S./A.E.S.
H.P.L.C. with anion separation column

Reagents

For the reagents needed for the different measurements of the separate ions, see below.

Procedures

1:5 extraction

Weigh 30 g (accuracy 0.1 g) of sample into a 250 ml shaking bottle. Add 150 ml water. Shake for 2 hours and allow to stand for another 2 hours. (If gypsum is expected in the soil, allow to stand overnight.) Filtrate over a hardened filter (e.g. Whatman 42). If the filtrate is turbid, filtrate again over the same filter. Measure pH, E.C., carbonate and bicarbonate immediately.

saturation extraction

Weigh at least 200 g of soil in a 1 litre beaker. For sandy soils, more sample will be needed to get enough extract. Add some water to saturate the soil and stir with a

stirring rod or spatula. Add some water if the paste is not yet saturated or add some soil if too much water was added to the soil.

A saturated soil is identified by the following criteria:
- when the beaker is tapped on the table, no water will appear at the soil surface
- the paste reflects light
- the paste flows slightly when the beaker is tipped
- the paste slides off the spatula cleanly and freely (not in case of heavy clays)

Cover the beaker and leave it overnight. It is best when the next day the paste seems just oversaturated. Adjust saturation when the paste does not meet the above criteria. Take some paste for moisture content determination and bring the rest of the paste to a Büchner funnel with a hardened filter. Filter off the soil moisture and measure pH, E.C., carbonate and bicarbonate immediately.

Measurements

moisture content (for saturation extract)

Place an empty crucible in the oven at 105° C and leave it there for at least 2 hours. Then place it in a desiccator and let it cool down.

Weigh the empty crucible (weight <u>A</u>). Weigh at least 2 g (accuracy 1 mg) of the saturation paste in the crucible and weigh it again (weight <u>B</u>). Place the crucible overnight in the oven at 105° C. Transfer the crucible to the desiccator and let it cool down. Finally, weigh the crucible again (weight <u>C</u>).

<u>Calculation of saturation percentage</u>

$$S.P.\ \textit{(saturation percentage)}\ (\%) = \frac{(B-C) \times 100\%}{(C-A)}$$

pH

<u>reagents</u>

Ampoules for buffers pH 4, 7 and 10.

Buffers for pH 4, 7 or 10

Dilute the respective ampoules according to the manufacturer's instructions.

Calibrate the pH meter according to the manufacturer's instructions, using the correct buffers (buffers 4 and 7 for pH $\leq$ 7 and buffers 7 and 10 for pH $\geq$ 7). Measure pH of the extract, reading 2 decimals.

electrical conductivity

<u>reagent</u>

Potassium chloride (KCl)

  test-solution

Weigh 372.8 mg or 745.5 mg of potassium chloride (dried at 105°C) into a 400 ml beaker. Dissolve it in water and transfer the solution to a 1 litre volumetric flask. Make up to volume with water and homogenize. The solution is 0.005 M or 0.010 M KCl respectively.

Fill the conductivity cell with the test-solution. Whether we use the 0.005 M KCl or the 0.010 M KCl test-solution, depends on the expected conductivity in the extract. Calibrate the conductivity meter according to the manufacturer's instructions. Rinse the conductivity cell three times with the extract to be measured and read the conductivity after a few minutes.

carbonate and bicarbonate

<u>reagents</u>

Ampoule for 0.01 M HCl
Ampoules for buffers pH 4 and 7

  0.01 M HCl

Dilute the ampoule according to manufacturer's instructions.

  Buffers of pH 4 and 7

Dilute the respective ampoules according to the manufacturer's instructions.

Pipette 10 ml extract in a 100 ml beaker. Add 20 ml freshly boiled (but cooled) water (also UHQ-water may used). Insert the glass electrode of the pH meter into the solution. Stir magnetically. Titrate with the 0.01 M HCl solution first to end-point pH=8.2. Read the volume for calculating the carbonate content. Thereafter, titrate to end-point 4.5. Read the volume for calculation of the bicarbonate content. Check calibration of the pH meter regularly.

calculation of carbonate and bicarbonate

1:5 extract

$$\text{carbonate } (mmol(-) \ kg^{-1}) = \frac{(V-B) \times t \times mcf \times 30,000}{W}$$

saturation extract

$$\text{carbonate } (mmol(-) \ kg^{-1}) = (V-B) \times t \times S.P. \times 2$$

---

where

V	= ml HCl used for carbonate in sample
B	= ml HCl used for carbonate in blank
t	= molarity of HCl
mcf	= moisture correction factor
W	= sample weight (g)
S.P.	= saturation percentage (%)
30,000	= conversion factor
2	= conversion factor

1:5 extract

$$\text{bicarbonate } (mmol(-) \ kg^{-1}) = \frac{(T-2V-B) \times t \times mcf \times 15,000}{W}$$

saturation extract

$$\text{bicarbonate } (mmol(-) \ kg^{-1}) = (T-2V-B) \times t \times S.P.$$

---

where

T	= ml HCl used for bicarbonate in sample
V	= ml HCl used for carbonate in sample
B	= ml HCl used for blank
t	= molarity of HCl
mcf	= moisture correction factor
W	= sample weight (g)
S.P.	= saturation percentage (%)
15,000	= conversion factor

Ca and Mg

reagents

Lanthanum oxide (La_2O_3) or lanthanum chloride ($LaCl_2.7\ H_2O$)
Hydrochloric acid 37% (HCl)
Ampoules for 1000 mg L^{-1} Ca and Mg

5% lanthanum solution

Weigh 58.6 gram of lanthanum oxide into a 1 litre beaker. Add about 800 ml water and carefully add 100 ml hydrochloric acid 37%. Allow the lanthanum oxide to dissolve (Alternatively, weigh in 133.7 g of lanthanum chloride and add 10 ml HCl 37%). Allow to cool and transfer the solution to a 1 litre measuring cylinder. Make up to volume with water and homogenize. If needed filter into a 1 litre polypropylene bottle.

1 M hydrochloric acid

Bring about 800 ml water to a 1 litre measuring cylinder. Carefully add 80 ml hydrochloric acid 37%. Make up to volume with water and homogenize.

1.25% lanthanum solution

Bring about 500 ml of water to a 1 litre measuring cylinder and add 250 ml of the 5% lanthanum solution. Add 15 ml 1 M HCl and make up to volume with water. Homogenize.

1000 mg L^{-1} standard solutions of Ca and Mg

Dilute the respective ampoules according to the manufacturer's instructions.

Standard series

Pipette 10 ml 1000 mg L^{-1} Mg-stock solution to a 100 ml volumetric flask. Make up to volume with water and homogenize. This solution is now 100 mg L^{-1} Mg.
Pipette 5 ml 1000 mg L^{-1} Ca-stock solution into a 100 ml volumetric flask. Pipette 5 ml of the 100 mg L^{-1} Mg-solution to the same volumetric flask. Make up to volume with water and homogenize. The mixed solution is now 50 mg L^{-1} Ca and 5 mg L^{-1} Mg.
Pipette from this mixed solution respectively 0, 5, 10 and 20 ml into 50 ml volumetric flasks. Add 10 ml 5% lanthanum-solution to each flask. Make up to volume with water and homogenize. The standard series is now:
Standard 1:   0.0 mg L^{-1} Ca and 0.00 mg L^{-1} Mg
Standard 2:   5.0 mg L^{-1} Ca and 0.50 mg L^{-1} Mg
Standard 3: 10.0 mg L^{-1} Ca and 1.00 mg L^{-1} Mg
Standard 4: 20.0 mg L^{-1} Ca and 2.00 mg L^{-1} Mg

Dilute the extract 1+4 with the 1.25 % lanthanum solution. Measure using the A.A.S. The wavelength for the Ca measurement is 422.7 nm and for the Mg measurement 285.2 nm. If the dilution of 5 times is not enough, dilute the extract again, but make sure that the matrix is 1% lanthanum and 0.02 M HCl.

Na and K

reagents

Cesium chloride (CsCl)
Hydrochloric acid 37% (HCl)
Ampoules for 1000 mg L^{-1} Na and K

10000 mg L^{-1} cesium solution

Weigh 12.7 g CsCl into a 150 ml beaker. Dissolve it in about 100 ml water. Transfer the solution to a 1 litre measuring cylinder and add 27 ml 37% HCl. Allow to cool and make up to 1 litre with water. Homogenize.

1250 mg L^{-1} cesium solution

Transfer 62.5 ml of the 10000 mg L^{-1} Cs solution to a 500 ml measuring cylinder. Make up to 500 ml with water and homogenize.

1000 mg L^{-1} standard solutions of K and Na

Dilute the respective ampoules according to manufacturer's instructions.

Standard series

Pipette 5 ml 1000 mg L^{-1} Na-stock solution to a 500 ml volumetric flask. Pipette 10 ml 1000 mg L^{-1} K-stock solution to the same volumetric flask. Make up to volume with water and homogenize. This mixed solution is now 10 mg L^{-1} Na and 20 mg L^{-1} K. Pipette from this mixed solution respectively 0, 5, 10 and 20 ml into 50 ml polypropylene volumetric flasks. Add 5 ml 10000 mg L^{-1} cesium solution to each flask. Make up to volume with water and homogenize.The standard series is now:

Standard 1: 0.0 mg L^{-1} Na and 0.0 mg L^{-1} K
Standard 2: 1.0 mg L^{-1} Na and 2.0 mg L^{-1} K
Standard 3: 2.0 mg L^{-1} Na and 4.0 mg L^{-1} K
Standard 4: 4.0 mg L^{-1} Na and 8.0 mg L^{-1} K

Dilute the extract 1+4 with the 1250 mg L^{-1} cesium solution. Measure using the A.E.S. The wavelength for the Na measurement is 589.0 nm and for the K measurement 766.5 nm. If the dilution of 5 times is not enough, dilute the extract again, but make sure that the background is 1000 mg L^{-1} cesium.

calculation of cations

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1:5 *extract*

$$Ca^{2+}, Mg^{2+}, Na^+ \text{ or } K^+ \text{ } (mmol(+) \text{ } kg^{-1}) = \frac{(C-B) \times D \times mcf \times 150}{W \times E}$$

saturation extract

$$Ca^{2+}, Mg^{2+}, Na^+ \text{ or } K^+ \text{ } (mmol(+) \text{ } kg^{-1}) = \frac{(C-B) \times D \times S.P.}{100 \times E}$$

</div>

where
C   = cation concentration in sample (mg L^{-1})
B   = cation concentration in blank (mg L^{-1})
D   = dilution factor
mcf   = moisture correction factor
W   = sample weight (g)
S.P. = saturation percentage (%)
150   = conversion factor
100^{-1} = conversion factor
E   = equivalent mass of cation
        E_{Ca}= 20.04 E_{Mg}= 12.16 E_{Na}= 22.99 E_K= 39.10

Cl, NO$_3$ and SO$_4$

reagents
Ultra High Quality (UHQ) water
Potassium hydrogenphthalate ($KH(C_8H_4O_4)$)
Ammonium hydroxide 25% (NH_4OH)
Sodium chloride (NaCl)
Sodium nitrate ($NaNO_3$)
Potassium sulphate (K_2SO_4)

   Eluent (20 mmol $KC_8H_5O_4$ per litre)

Weigh 8.0 g potassium hydrogenphthalate in a 1 litre beaker. Dissolve in UHQ-water. Transfer the solution to a 2 litre volumetric flask. Add 10 drops of ammonium hydroxide (25%). Make up to volume with UHQ-water and homogenize. The pH should be 4.0. Filter over a 0.45 μm membran filter using a clarification kit.

   1.000 gram chloride per litre stock solution

Weigh 1.6484 g sodium chloride (dried at 105°C) in a 400 ml beaker. Dissolve in about 300 ml UHQ-water. Transfer to a 1 litre volumetric flask. Make up to volume with UHQ-water and homogenize.

1.000 gram nitrate per litre stock solution

Weigh 1.3707 g sodium nitrate (dried at 105° C) in a 400 ml beaker. Dissolve in about 300 ml UHQ-water. Transfer the solution to a 1 litre volumetric flask. Make up to volume with UHQ-water and homogenize.

1.000 gram sulphate per litre stock solution

Weigh 1.8142 gram potassium sulphate (dried at 105° C) in a 400 ml beaker. Dissolve in about 300 ml UHQ-water. Transfer the solution to 1 litre volumetric flask. Make up to volume with UHQ-water and homogenize.

<u>standard series</u>

Pipette respectively 15 ml chloride stock solution, 30 ml nitrate stock solution and 30 ml sulphate stock solution into a 500 ml volumetric flask. Make up to volume with UHQ-water and homogenize. This combined standard solution is 30 mg L^{-1} Cl, 60 mg L^{-1} NO_3 and 60 mg L^{-1} SO_4 (standard 7).
Pipette from the combined standard solution respectively 0, 5, 10, 20, 30 and 40 ml in 50 ml volumetric flasks. Make up to volume with UHQ-water and homogenize. The standard series is now:

Standard 1:   0.0 mg L^{-1} Cl^-,   0.0 mg L^{-1} NO_3^- 0.0 mg L^{-1} SO_4^{2-}
Standard 2:   3.0 mg L^{-1} Cl^-,   6.0 mg L^{-1} NO_3^- 6.0 mg L^{-1} SO_4^{2-}
Standard 3:   6.0 mg L^{-1} Cl^-,   12.0 mg L^{-1} NO_3^- 12.0 mg L^{-1} SO_4^{2-}
Standard 4: 12.0 mg L^{-1} Cl^-,   24.0 mg L^{-1} NO_3^- 24.0 mg L^{-1} SO_4^{2-}
Standard 5: 18.0 mg L^{-1} Cl^-,   36.0 mg L^{-1} NO_3^- 36.0 mg L^{-1} SO_4^{2-}
Standard 6: 24.0 mg L^{-1} Cl^-,   48.0 mg L^{-1} NO_3^- 48.0 mg L^{-1} SO_4^{2-}
Standard 7: 30.0 mg L^{-1} Cl^-,   60.0 mg L^{-1} NO_3^- 60.0 mg L^{-1} SO_4^{2-}

Let the H.P.L.C. stabilize with a pump speed of 0.4 ml per minute. Adjust the temperature of the refractometer to 35°C and the temperature control module to 38°C. Filter the samples over a 0.2μm filter to prevent clocking of the system. Run standards and samples automatically, following the manufacturer's instructions.

<u>calculations of anions</u>

1:5 extract

$$Cl^-,\ NO_3^-\ or\ SO_4^{2-}\ (mmol(-)\ kg^{-1}) = \frac{(C-B) \times D \times mcf \times 150}{W \times E}$$

saturation extract

$$Cl^-,\ NO_3^-\ or\ SO_4^{2-}\ (mmol(-)\ kg^{-1}) = \frac{(C-B) \times D \times S.P.}{100 \times E}$$

where

C	= anion concentration in sample (mg L^{-1})	
B	= anion concentration in blank (mg L^{-1})	
D	= dilution factor	
mcf	= moisture correction factor	
W	= sample weight (g)	
S.P.	= saturation percentage (%)	
150	= conversion factor	
100^{-1}	= conversion factor	
E	= equivalent mass of anion	

$$E_{Cl} = 35.45$$
$$E_{NO3} = 62.01$$
$$E_{SO4} = 48.03$$

Remarks

- Instead of the pH-meter, an indicator may be used as end-point detector for the titrations. Use phenolphthalein and methyl orange for, respectively, carbonate and bicarbonate.

- Instead of pH-meter and burette, an automatic titrator may be used for the titrations.

References

- Van Reeuwijk, L.P., 1992. Procedures for Soil Analysis. I.S.R.I.C. Technical Paper no. 9, 3rd ed., chapter 13.

- Velthorst, E.J., 1993. Manual for Chemical Water Analyses. Department of Soil Science and Geology, Agricultural University Wageningen.

- Velthorst, E.J. and B. van Lagen, 1992. Optimisation of Na and K measurement with AES. Intern verslag no 56. Department of Soil Science and Geology, Agricultural University, Wageningen (in Dutch).

A21: IRON (II) AND IRON (III)

Principle

The sample is destructed with a mixture of hydrofluoric and sulphuric acid. By creating optimal conditions, the iron in the sample will reduce nor oxidize. Iron (II) is determined with o-phenanthroline as the colouring reagent. Total iron is determined subsequently after reducing iron (III) to iron (II) by hydroquinone. The difference between total iron and iron (II) is iron (III).

Apparatus

Pt-crucible of 35 ml
Dispensers for 5 ml
Quartz beaker of 100 ml
Hot plate
Spectrophotometer

Reagents

Sulphuric acid 96% (H_2SO_4)
Hydrofluoric acid 48% (HF)
Boric acid (H_3BO_3)
Hydrochloric acid 37% HCl)
Potassium hydrogenphthalate ($KH(C_8H_4O_4)$)
1,10-orthophenantroline ($C_{12}H_9N_2Cl.H_2O$)
Hydroquinone ($C_6H_4(OH)_2$)
Ampoule for 1000 mg L^{-1} Fe

4% boric acid

Dissolve 40 g H_3BO_3 in 1 litre water.

4 M hydrochloric acid

Carefully add 80 ml HCl (37%) to 150 ml water. Allow to cool and make up to 250 ml with water. Homogenize.

0.5 M potassium hydrogenphthalate buffer

Dissolve 25 g $KH(C_8H_4O_4)$ in 200 ml water by heating it. Allow to cool and make up to 250 ml with water. Homogenize.

0.25% 1,10-orthophenantroline

Dissolve 250 mg $C_{12}H_9N_2Cl.H_2O$ in 100 ml water.

1000 mg L^{-1} Fe stock solution

Dilute an ampoule for 1000 mg L^{-1} Fe according to the manufacturer's instructions.

Standard series

Pipette 25 ml of the 1000 mg L^{-1} Fe stock solution into a 250 ml volumetric flask. Make up to volume with water and homogenize. This solution is now 100 mg L^{-1} Fe (= standard 6).
Pipette respectively 0, 10, 20, 30 and 40 ml of the 100 mg L^{-1} Fe solution to 50 ml volumetric flasks. Make each flask up to volume with water and homogenize. The standard series is now: Standard 1: 0 mg L^{-1} Fe
Standard 2: 20 mg L^{-1} Fe
Standard 3: 40 mg L^{-1} Fe
Standard 4: 60 mg L^{-1} Fe
Standard 5: 80 mg L^{-1} Fe
Standard 6:100 mg L^{-1} Fe

Procedure

Weigh 100 mg (accuracy 0.1 mg) ground sample into a 35 ml Pt-crucible. Add 1.0 ml H_2SO_4 96% using a dispenser and mix. Add 3.0 ml HF 48%, using a polypropyleen dispenser and swirl for 10 seconds. Immediately transfer the contents of the crucible with water to a 100 ml quartz beaker, containing 10 ml boric acid solution and 3 ml 4 M HCl. Place a polypropylene cover on the beaker and place it on the hot plate. Boil gently for 2 minutes. Allow to cool and transfer the contents to a 100 ml polypropylene volumetric flask, which contains 40 ml boric acid solution. Make up to volume with water and homogenize.
Filtrate the destruate in a polypropylene bottle using a polypropylene funnel. The measurement of Fe^{2+} should be done as soon as possible.

Measurement

Measurement of Fe^{2+}

Pipette 1 ml of the standard series or of the sample into a 25 ml volumetric flask. Add about 15 ml water and 5.0 ml of the potassium hydrogenphthalate buffer using a dispensette. Mix and add 2.0 ml of the 1,10-orthophenantroline. Make up to volume with water and homogenize. Measure the absorbance within 15 minutes at a wavelength of 515 nm.

Measurement of Fe^{2+} and Fe^{3+}

After the measurement of Fe^{2+}, add about 10 mg solid hydroquinone to each volumetric flask. Mix, allow to stand for at least 30 minutes, and again measure the absorbance at 515 nm.

Calculation

Prepare a plot of Fe-concentration against absorbance. Read or calculate the Fe concentration of the sample from this plot.

$$Fe^{2+} \text{ or } (Fe^{2+} + Fe^{3+}) \text{ (\%)} = \frac{(C-B) \times 10 \times mcf}{W}$$

$$Fe^{3+} \text{ (\%)} = (Fe^{2+} + Fe^{3+}) \text{ (\%)} - Fe^{2+} \text{ (\%)}$$

where

C   = Fe concentration in the sample (mg L^{-1})
B   = Fe concentration in the blank (mg L^{-1})
mcf = moisture correction factor
W   = sample weight (mg)
10 = conversion factor

Remarks

-   Because the moisture content may change by grinding, execute another moisture analysis to determine the moisture correction factor.

-   Because HF is used in this procedure, take safety precautions (e.g. wear rubber gloves and work in a fumeboard).

-   According to Jeffery et al. (1989), the total of $Fe^{2+} + Fe^{3+}$ can also be measured at 396 nm without adding hydroquinone. Because of the matrix of the samples, this is not possible (van Lagen,1992).

-   In case of acid sulphate soils, the residue obtained after HF destruction may be used for the determination of pyrite. In that case, filtration should be replaced by centrifugation and washing.

References

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- Jeffery, G.H., J. Bassett, J. Mendham and R.C. Denney., 1989. Vogel's Textbook of Quantitative Chemical Analysis. 5th ed., page 690-692.

- Van Lagen, B., 1992. Iron measurement for the analysis of Fe^{2+} and Fe^{3+}. Intern Verslag no 54. Department of Soil Science and Geology, Agricultural University Wageningen.

GENERAL SULPHUR FRACTIONATION

Three procedures for analyzing sulphur fractions are described here.

- Total sulphur after oxidation and reduction

- HI-reducible sulphur for inorganic, ester-bound and part of the elementary sulphur and Fe(II)sulphide

- Raney-Nickel reducible sulphur for parts of the organically bound sulphur

A22: TOTAL SULPHUR

Principle

The sulphur in a sample is oxidized with an alkaline sodium hypobromite solution. The formed sulphate is reduced with hydriodic acid. The formed hydrogen sulphide is trapped in sodium hydroxide and measured turbidimetrically with bismuth as reagent.

Apparatus

Magnetic stirrer
Kjehldahl destruction assembly
Reagent preparation apparatus (see figure 4)
Destruction-distillation apparatus (see figure 5)
Variable micro-pipette (0-1000 µl)
Dispenser for 5 ml
Spectrophotometer

Reagents

Bromine (Suprapur) (Br_2)
Sodium hydroxide (NaOH)
Formic acid >98% (HCOOH)
Hydriodic acid 57% (HI)
Hypophosphorous acid 50% (H_3PO_2)
Bismuth(III) nitrate ($Bi(NO_3)_3$)
Acetic acid glacial (CH_3COOH)
Gelatin
Potassium sulphate (K_2SO_4)
p-Nitrophenyl sulphate potassium salt ($C_6H_4NO_6SK$) (Sigma N-3877)

> 2 M sodium hydroxide

Dissolve 80 g NaOH in 1 litre distilled water. Store in a polythene flask.

> sodium hypobromide solution

Add 100 ml 2 M NaOH solution to a 150 ml beaker. While stirring magnetically, carefully add (with a rate of approx. 0.5 ml per minute) 3 ml Br_2. Use a plastic syringe for this. Place a cover on the beaker. **(This solution must be made immediately before using it.)**

> HI-reducing reagent

Assemble the preparation apparatus for HI preparation according to Figure 5. Add to the three-neck roundbottom flask, by using a measuring cylinder, successively 100 ml HI, 50 ml HCOOH and 25 ml H_3PO_2. Mix and boil the mixture for 1 hour under a gentle flow of very pure nitrogen (flow = 1 bubble per second).

attention: Keep temperature under 117° C, because of formation of poisonous phosphine gas (PH$_3$). Check nitrogen-flow regularly. This solution can be kept for about 2 weeks. **Keep in the dark and away from air as much as possible.**

1 M sodium hydroxide

Dissolve 40 g of NaOH in 1 litre water. Keep this solution in a polythene flask.

bismuth reagent

Bring 230 ml acetic acid glacial in a 500 ml beaker. Add 2.0 g Bi(NO$_3$)$_3$. Heat to a temperature between 80 and 100° C until the Bi(NO$_3$)$_3$ has dissolved. Allow to cool.

Boil 400 ml water in a 1 litre beaker. Remove the heater and add 30 g of gelatin. Stir till the gelatin has dissolved.

Place a glass funnel with a Whatman no. 50 (or similar) filter paper on a 1 litre volumetric flask. Filtrate the bismuth solution. After filtration, clean the funnel with water and add the warm gelatin solution to the filtrated bismuth solution. Stir this mixture overnight using a magnetic stirrer. The next day, remove and clean the stirring rod. Make up to volume with water and homogenize. This solution is stable indefinitely.

Standard series

Weigh 679.3 mg K$_2$SO$_4$ (dried at 105° C) in a 150 ml beaker. Dissolve in 100 ml water and transfer to a 250 ml volumetric flask. Make up to volume and homogenize. This solution is now 500 mg l^{-1} S.

Pipette 10 ml of this 500 mg l^{-1} S-solution into a 100 ml volumetric flask. Make up to volume with water and homogenize. This solution is now 50 mg l^{-1} S.

To make the final standard series 0, 200, 400, 600, 800 and 1000 µl are pipetted into the destruction tube (tube E, fig 5) and treated as the samples. The standard series is then:

standard 1: 0 µg S
standard 2: 10 µg S
standard 3: 20 µg S
standard 4: 30 µg S
standard 5: 40 µg S
standard 6: 50 µg S

Procedure

Oxidation

Weigh 100 mg (accuracy 0.1 mg) of freeze-dried and ground sample into the destruction tube (tube E in Fig 5). Add 3 ml of the sodium hypobromide solution and swirl for a few seconds. Allow the tube to stand for 5 minutes and swirl again for a few seconds. Place the tube in the pre-heated Kjehldahl destruction assembly (temp=250-260° C). Evaporate the hypobromide solution (beware of foaming). Leave the tube another 30 minutes in the hot destruction assembly. Remove the tube and allow to

cool for 5 minutes. Add 1 ml water and heat for a few seconds to suspend the residue. Allow to cool. Less than 2 hours before the reduction, add 1 ml formic acid (>98%) to destruct the hypobromide and make sure that pH is below 7.

Reduction

Assemble a destruction-distillation apparatus according to figure 5. Pipette 5 ml 1 M NaOH in the absorption tube (tube G). Pipette one of the standards in the destruction tube (tube E) or use an oxidized sample. Fit the tube in the apparatus and flush for 1 minute with nitrogen, using a flow of 1 bubble per second. Add 4 ml HI-reducing reagent to the destruction tube (tube E) via the separation funnel (funnel F) (Do this as fast as possible to minimize contact between reagent and air). Flush again for 1 minute with nitrogen. Bring the mixture in the destruction tube quickly to boiling, with the micro-burner (J). When the mixture is boiling, place the pre-heated hot plate (plate H) under the tube and cover the plate with the heat shield (shield I). Adjust the nitrogen-flow again to 1 bubble per second. Destruct and distill for 30 minutes. After this time, remove the absorption-tube (tube G) and add 2.5 ml of the bismuth reagent, using a 5 ml dispenser. Homogenize. This solution can be kept till the end of the day. Clean the apparatus with water and carefully dry the fittings and the gas-dispersion tube before the next sample is treated.

Measurement

At the end of the day, the absorbance of the collected samples and standard solutions can be measured by spectrophotometer at a wavelength of 400 nm.

Calculation

Prepare a plot of sulphur weight against absorbance. Read or calculate the sulphur weight (μg) of the sample from this plot.

$$Total\ sulphur\ (mmol\ kg^{-1}) = \frac{(C-B) \times 31.186 \times mcf}{W}$$

where

C   = sulphur weight of the sample (μg)
B   = sulphur weight of the blank (μg)
mcf   = moisture correction factor
W   = sample weight (mg)
31.186 = conversion factor

Remarks

- Use distilled water throughout the procedure.

- The samples have to be freeze-dried to prevent transformation of S-compounds in the soil.

- The sample must contain less than 40 µg S. If 100 mg of sample contains more than 12.5 mmol total S kg^{-1}, use less material.

- Start the day with a blank analysis to clean the apparatus.

- Treat the samples and the standards in a random sequence through the day.

- Because reference samples are not present for this procedure, take an S-containing chemical instead, for example the potassium salt of para-nitrophenylsulphate (PNPS). Dissolve 200 mg PNPS in 150 ml water. Transfer to a 250 ml volumetric flask, make up to volume with water and homogenize. This solution contains 100 mg l^{-1} S. Pipette 300 µl as sample in the destruction-tube (tube E). Also L-methionine or potassium sulphate may be used.

- Take every possible safety precaution to avoid damage to man and the environment. Work in a fume cupboard, use as few chemicals as possible etc.

- After cleaning, the destruction tubes may look dirty, but this is because of etching of the glass by the sodium hypobromide.

- When using a double destruction/destillation set-up, the capacity is about 5 standards, 2 blanks and 10 samples per day.

References

- Dean, G.A., 1966. A simple colorimetric finish for the Johnston-Nishita micro-distillation of sulphur. Analyst 91:530-532.

- Kowalenko, C.G., 1985. A modified apparatus for quick and versatile sulphate sulphur analysis using hydriodic acid reduction. Communications in Soil Science and Plant Analysis 16(3):289-300.

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- Tabatabai, M.A., 1982. Sulphur. in: Methods of Soil Analysis. part 2 - Chemical and Microbiological Properties, Agronomy No.9, 2nd ed., page 501-538.

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Figure 5: Apparatus for preparing the HI-reducing reagent.
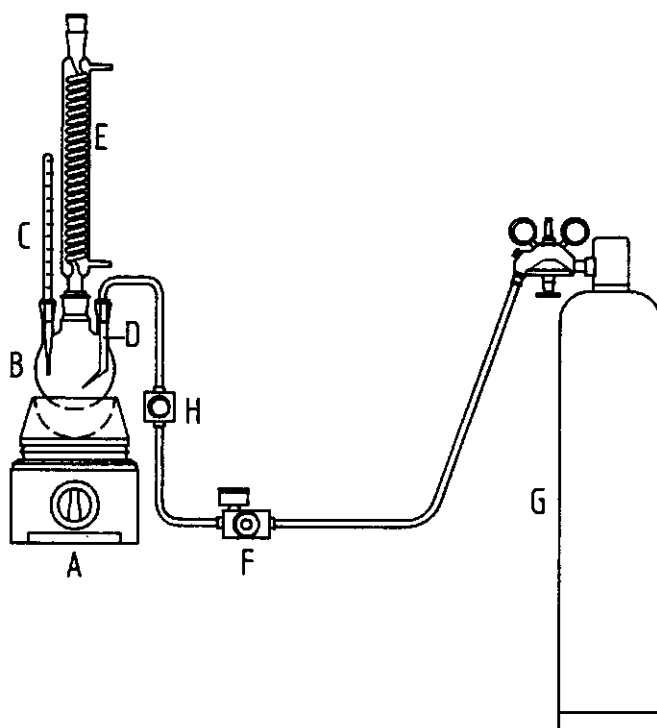
A: hot plate.
B: three-neck roundbottom flask.
C: thermometer (>100°C)
D: nitrogen inlet tube.
E: condenser.
F: reducing valve (0-10 atm).
G: gas cylinder for very pure nitrogen (N_2>99.99%) with reducing valve.
H: precision gas pressure regulator.

Figure 6: Destruction and distillation apparatus.
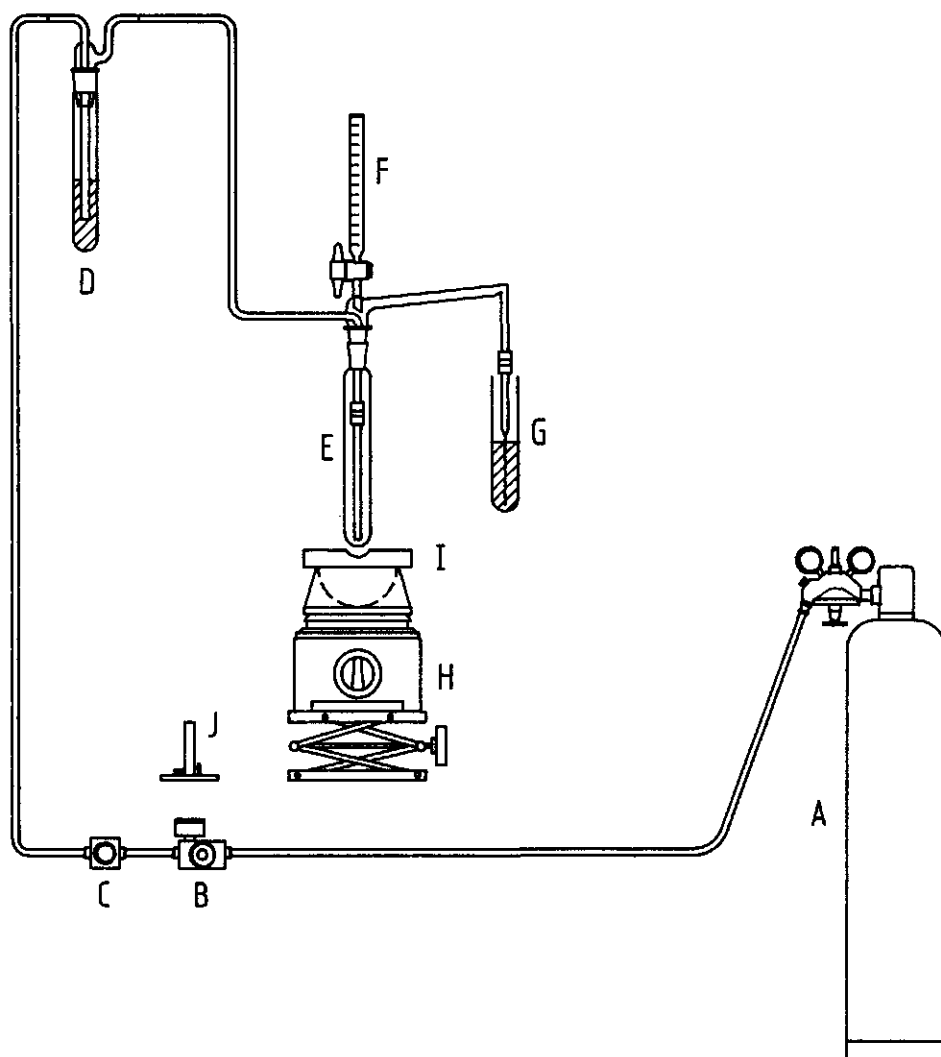
A: gas cylinder for very pure nitrogen (N$_2$>99.99%) with reducing valve.
B: reducing valve (0-10 atm).
C: precision gas pressure regulator.
D: gas washing bottle filled with distilled water. (=bubble counter)
E: Taylor destruction tube.
F: 10 ml separating funnel with teflon stopcock.
G: absorption unit consisting of a 10 ml glass tube and a gas-dispersion tube.
H: Hot plate
I: Heat shield of metal wire and glasswool (with a hole for the destruction tube.)
J: Micro burner.

A23: HI-REDUCIBLE SULPHUR

Principle

Inorganic, ester-bound and part of the elementary sulphur and iron(II)sulphide is reduced by a mixture of hydriodic acid, formic acid and hypophosphorous acid. The formed hydrogen sulphide is trapped in a sodium hydroxide solution and measured turbidimetrically by a bismuth reagent.

Apparatus

Reagent preparation apparatus (see Figure 6)
Magnetic stirrer
Destruction-distillation apparatus (see Figure 7)
Variable micro-pipette (0-1000 µl)
Dispenser for 5 ml
Spectrophotometer

Reagents

Hydriodic acid 57% (HI)
Formic acid >98% (HCOOH)
Hypophosphorous acid 50% (H_3PO_2)
Sodium hydroxide (NaOH)
Bismuth(III) nitrate ($Bi(NO_3)_3$)
Acetic acid glacial (CH_3COOH)
Gelatin
Potassium sulphate (K_2SO_4)
p-Nitrophenyl sulphate potassium salt ($C_6H_4NO_6SK$) (Sigma N-3877)

HI-reducing reagent

Assemble the preparation apparatus according to Figure 6. Add to the three-neck roundbottom flask, using a measuring cylinder, successively 100 ml HI, 50 ml HCOOH and 25 ml H_3PO_2. Mix and boil the mixture for 1 hour under a gentle flow of very pure nitrogen (flow = 1 bubble per second).
Attention: Keep temperature under 117° C, because of formation of poisonous phosphine gas (PH_3). Check nitrogen-flow regularly. This solution can be kept for about 2 weeks. **Keep in the dark and away from air as much as possible.**

1 M sodium hydroxide

Dissolve 40 g of NaOH in 1 litre distilled water. Keep this solution in a polythene flask.

Bismuth reagent

Bring 230 ml acetic acid glacial in a 500 ml beaker. Add 2.0 g Bi(NO$_3$)$_3$. Heat to a temperature between 80 and 100°C till the Bi(NO$_3$)$_3$ has dissolved. Allow to cool.

Boil 400 ml water in a 1 litre beaker. Remove the heater and add 30 g of gelatin. Stir till the gelatin has dissolved. Place a glass funnel with a Whatman no. 50 (or similar) filterpaper on a 1 litre volumetric flask. Filtrate the bismuth solution. Clean the funnel after filtration with water and add the warm gelatin solution to the filtrated bismuth solution. Stir this mixture overnight using a magnetic stirrer. The next day remove and clean the stirring rod. Make the flask to volume with water and homogenize. This solution is stable indefinitely.

Standard series

Weigh 679.3 mg K$_2$SO$_4$ (dried at 105°C) in a 150 ml beaker. Dissolve in 100 ml water and transfer to a 250 ml volumetric flask. Make up to volume and homogenize. This makes a 500 mg l^{-1} S solution.

Pipette 10 ml of the 500 mg l^{-1} S solution into a 100 ml volumetric flask. Make up to volume with water and homogenize. This makes a 50 mg l^{-1} S solution.

To make the final standard series 0, 200, 400, 600, 800 and 1000 µl, respectively, are pipetted into the destruction tube (tube E, fig 7) and processed as the samples. The standard series is then:

standard 1:   0 µg S
standard 2: 10 µg S
standard 3: 20 µg S
standard 4: 30 µg S
standard 5: 40 µg S
standard 6: 50 µg S

Procedure

Assemble a destruction-distillation apparatus according to figure 7. Pipette 5 ml 1 M NaOH in the absorption tube (tube G). Pipette a standard in the destruction tube (tube E) or weigh 100 mg (accuracy 0.1 mg) of freeze-dried and ground sample in this tube. Fit the tube in the apparatus and flush for 1 minute with a nitrogen flow of 1 bubble per second. Add 4 ml HI-reducing reagent to the destruction tube (tube E) via the separation funnel (funnel F). Do this as fast as possible to minimize contact between reagent and air. Flush again for 1 minute with nitrogen. Bring the mixture in the destruction tube quickly to boiling with the micro-burner (burner J). When the mixture is boiling, place the pre-heated hot plate (plate H) under the tube and cover the plate with the heat shield (shield I). Adjust the nitrogen flow again to 1 bubble per second. Destruct and distill for 30 minutes. Then, remove the absorption-tube (tube G) and add, using a 5 ml dispenser, 2.5 ml of the bismuth reagent. Homogenize. This solution can be kept till the end of the day. Clean the apparatus with water and carefully dry the fittings and the gas-dispersion tube before processing the next samples.

Measurement

At the end of the day, the absorbance of the collected samples and standard solutions can be measured by spectrophotometer at a wavelength of 400 nm.

Calculation

Prepare a plot of sulphur weight against absorbance. Read or calculate the sulphur weight (μg) of the sample from this plot.

$$\text{HI-reducible sulphur (mmol kg}^{-1}) = \frac{(C-B) \times 31.186 \times mcf}{W}$$

where

C	= sulphur weight of the sample (μg)
B	= sulphur weight of the blank (μg)
mcf	= moisture correction factor
W	= sample weight (mg)
31.186	= conversion factor

Remarks

- Use distilled water throughout the procedure.

- The samples have to be freeze-dried to prevent transformation of S compounds in the soil.

- The sample must contain less the 40 μg S. If 100 mg of sample contains more than 12.5 mmol HI-reducible S kg^{-1}, use less material.

- Moisten samples rich in organic matter with a few drops of the HI-reducing reagent _just before_ the destruction tube is fitted in the apparatus. This avoids floating of the sample on the reagent.

- Start every day with a blank analysis to clean the apparatus.

- Treat the samples and the standards in a random sequence through the day.

- Because reference samples are not present for this procedure, take an S containing chemical instead, for example the potassium salt of para-

nitrophenylsulphate (PNPS). Dissolve 200 mg PNPS in 150 ml water. Transfer to a 250 ml volumetric flask. Make up to volume with water and homogenize. This solution contains 100 mg l^{-1} S. Pipette 300 µl as sample in the destruction-tube (tube E).

- Take every possible safety precaution to avoid damage to man and to the environment. Work in a fume cupboard, use as few chemicals as possible etc.

- When using a double destruction/destillation set-up, the capacity is about 5 standards, 2 blanks and 10 samples per day.

References

- Dean, G.A., 1966. A simple colorimetric finish for the Johnston-Nishita micro-distillation of sulphur. Analyst 91:530-532.

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A24: RANEY-NICKEL-REDUCIBLE SULPHUR

Principle

Part of the organically bound sulphur is reduced by a mixture of elementary nickel and aluminium (Raney-Nickel powder) and sodium hydroxide. By the formation of catalytic nickel the carbon bound sulphur is reduced to sulphide. After neutralizing the reduction solution with hydrochloric acid, the formed hydrogen sulphide is distilled and trapped in sodium hydroxide. The sulphide is measured turbidimetrically with bismuth as reagent.

Apparatus

Destruction-distillation apparatus (see figure 8)
10 ml plastic syringe with removable needle
Dispenser for 5 ml
Spectrophotometer

Reagents

Sodium hydroxide (NaOH)
Nickel-aluminium alloy powder (50% Ni and 50% Al)
Isoamyl alcohol (3-methyl-1-butanol) ($C_5H_{11}OH$)
Hydrochloric acid 37% (HCl)
Bismuth(III) nitrate ($Bi(NO_3)_3$)
Acetic acid glacial (CH_3COOH)
Gelatin
Sodium thiosulphate ($Na_2S_2O_3.5H_2O$)
L-methionine (DL-2-amino-4-[methylthio]--butanoic acid) ($C_5H_{11}NO_2S$) (Sigma M-9625)

      5% sodium hydroxide

Dissolve 50 g NaOH in 1 litre distilled water. Keep in a polythene flask.

      1 M sodium hydroxide

Dissolve 40 g of NaOH in 1 litre water. Keep this solution in a polythene flask.

      20% hydrochloric acid

Add 540 ml HCl 37% to 400 ml water. Allow to cool and make up to 1 litre with water. Homogenize.

      Bismuth reagent

Pour 230 ml acetic acid glacial into a 500 ml beaker. Add 2.0 g $Bi(NO_3)_3$. Heat to a temperature

between 80 and 100° C until the $Bi(NO_3)_3$ has dissolved. Allow to cool.
Boil 400 ml water in a 1 litre beaker. Remove the heater and add 30 g of gelatin. Stir until the gelatin has dissolved. Place a glass funnel with a Whatman no. 50 (or similar) filterpaper on a 1 litre volumetric flask. Filtrate the bismuth solution. Clean the funnel after filtration with water and add the warm gelatin solution to the filtrated bismuth solution. Stir this mixture overnight using a magnetic stirrer. The next day, remove and clean the stirring rod. Make the flask up to volume with water and homogenize. This solution is stable indefinitely.

Standard series

Weigh 193.5 mg $Na_2S_2O_3.5H_2O$ into a 150 ml beaker. Dissolve in 100 ml water. Transfer the solution to a 1 litre volumetric flask. Make up to volume with water and homogenize. This standard solution is 50 mg l^{-1} S. To make the final standard series 0, 200, 400, 600, 800 and 1000 µl, respectively, are pipetted into the reaction flask (flask A, fig 8) and treated as a sample. The standard series is then:
standard 1:   0 µg S
standard 2: 10 µg S
standard 3: 20 µg S
standard 4: 30 µg S
standard 5: 40 µg S
standard 6: 50 µg S

Procedure

Assemble the destruction-distillation apparatus according to figure 8.

Destruction

Pipette 5 ml 5% NaOH solution into the roundbottom flask (flask A). Add about 100 mg nickel aluminium alloy powder. Pipette one of the standards or weigh 100 mg (accuracy 0.1 mg) of sample in the roundbottom flask. Add 3 drops of isoamyl alcohol. Add 25 ml of water using a measuring cylinder. Fit the roundbottom flask in the apparatus. Flush for 1 minute with nitrogen (flow is 1 bubble per second). Start to cool. Place the pre-heated hot plate under the roundbottom flask. Bring the solution to boiling. Boil for 30 minutes. Increase the nitrogen-flow to 2-3 bubbles per second. Remove the hot plate. Allow to cool for 5 minutes.

Distillation

Pipette 5 ml 1 M NaOH into the absorption tube (tube C) and fit the tube in the apparatus. Prevent suction of the sodium hydroxide solution into the gas dispersion tube by adjusting the nitrogen-flow. Remove the needle from the syringe. Fill the syringe with about 6 ml 20% HCl solution. Re-install the needle and remove the air from the syringe. Adjust the volume to 5 ml. Decrease the nitrogen-flow to 1 bubble per 2 seconds. Insert the needle through the septum of the roundbottom flask and

inject the HCl solution quickly. Withdraw the syringe and adjust the nitrogen flow to 1 bubble per second. Re-install the pre-heated hot plate and bring the solution to boiling. Boil for 15 minutes with a nitrogen flow of 1 bubble per second. Re-adjust the nitrogen-flow to 2 bubbles per second and boil for another 15 minutes. Remove the absorption tube (tube C) and add 2.5 ml of the bismuth colouring reagent using the dispensette. Homogenize. This solution can be kept till the end of the day. Clean the apparatus with water and carefully dry the fittings and the gas-dispersion tube before processing the next samples.

Measurement

At the end of the day the absorbance of the collected samples and standard solutions can be measured by spectrophotometer at a wavelength of 400 nm.

Calculation

Prepare a plot of sulphur weight against absorbance. Read or calculate the sulphur weight (μg) of the sample from this plot.

$$\text{Raney nickel reducible sulphur (mmol kg}^{-1}) = \frac{(C-B) \times 31.186 \times mcf}{W}$$

where

C   = sulphur weight of the sample (μg)
B   = sulphur weight of the blank (μg)
mcf   = moisture correction factor
W   = sample weight (mg)
31.186 = conversion factor

Remarks

-        Use distilled water throughout the procedure.

-        At the end of the distillation remove the absorption tube before removing the hot plate to prevent suction of the sodium hydroxide solution in it.

-        The samples have to be freeze-dried to prevent transformation of S-compounds in the soil.

-        Isoamyl alcohol prevents foaming during destruction and distillation. Beware of inhalation of the vapours of this alcohol. It is very poisonous.

- The sample must contain less than 40 µg S. If 100 mg of sample contains more than 12.5 mmol Raney-nickel-reducible S kg^{-1}, use less material.

- Start the day with a blank analysis to clean the apparatus.

- Treat the samples and the standards in a random sequence through the day.

- Because reference samples are not present for this procedure, take an S-containing chemical instead, for example L-methionine. Dissolve 116.3 mg of L-methionine in 350 ml water. Transfer to a 500 ml volumetric flask. Make up to volume with water and homogenize. This solution contains 50 mg l^{-1} S. Pipette 600 µl as sample in the destruction-tube (tube E).

- Take every possible safety precaution to avoid damage to man and to the environment. Work in a fume cupboard, use as few chemicals as possible, etc.

- When using 3 destruction/destillation set-ups the capacity is about 5 standards, 2 blanks and 8 samples per day.

References

- Dean, G.A., 1966. A simple colorimetric finish for the Johnston-Nishita micro-distillation of sulphur. Analyst 91:530-532.

- DeLong, W.A., and L.E. Lowe, 1962. Note on carbon bounded sulphur soil. Canadian Journal of Soil Science 42:223.

- Freney, J.R., G.E. Melville and C.H. Williams, 1970. The determination of carbon bounded sulphur in soil. Soil Science 109(5):310-318.

- Kowalenko, C.G., and L.E. Lowe, 1972. Observations on the bismuth sulphide colorimetric procedure for sulphate analysis in soil. Communications in Soil and Plant Analysis 3(1):79-86.

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- Tabatabai, M.A., 1982. Sulphur. in: Methods of Soil Analysis. part 2 - Chemical and Microbiological Properties, Agronomy No.9, 2nd ed., page 501-538.

Figure 9: Destruction and distillation apparatus.
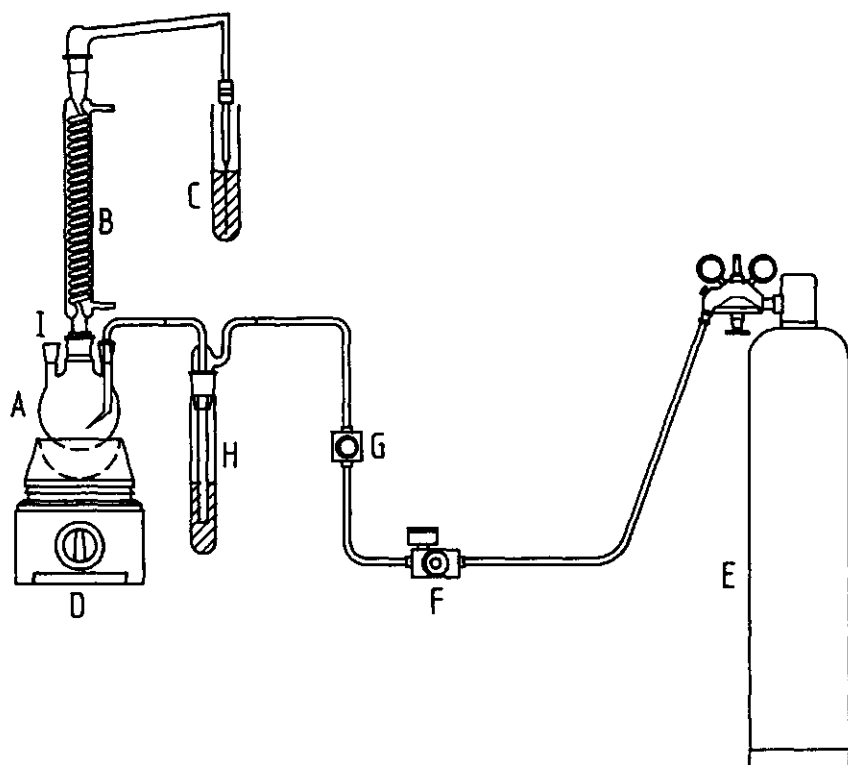
A: three-neck round bottom flask of 250 ml.
B: cooler.
C: absorption unit consisting of a 10 ml glass tube and a gas-dispersion tube.
D: hot plate
E: gas cylinder for very pure nitrogen (N_2>99.99%) with reducing valve.
F: reducing valve (0-10 atm).
G: precision gas pressure regulator.
H: gas washing bottle filled with distilled water (=bubble-counter).
I: plastic stopcock with septum.

SULPHUR FRACTIONATION FOR ACID SULPHATE SOILS

The procedures described next are developed at the department of Soil Science and Geology of the Agricultural University of Wageningen especially for research on acid sulphate soils. It seperates the sulphur content of these soils in different fractions. For analysis scheme see fig 9.

Figure 10: Analytical scheme for sulphur fractionation in acid sulphate soils.

Figure 10 : (continued): Analytical scheme for sulphur fractionation in acid sulphate soils.
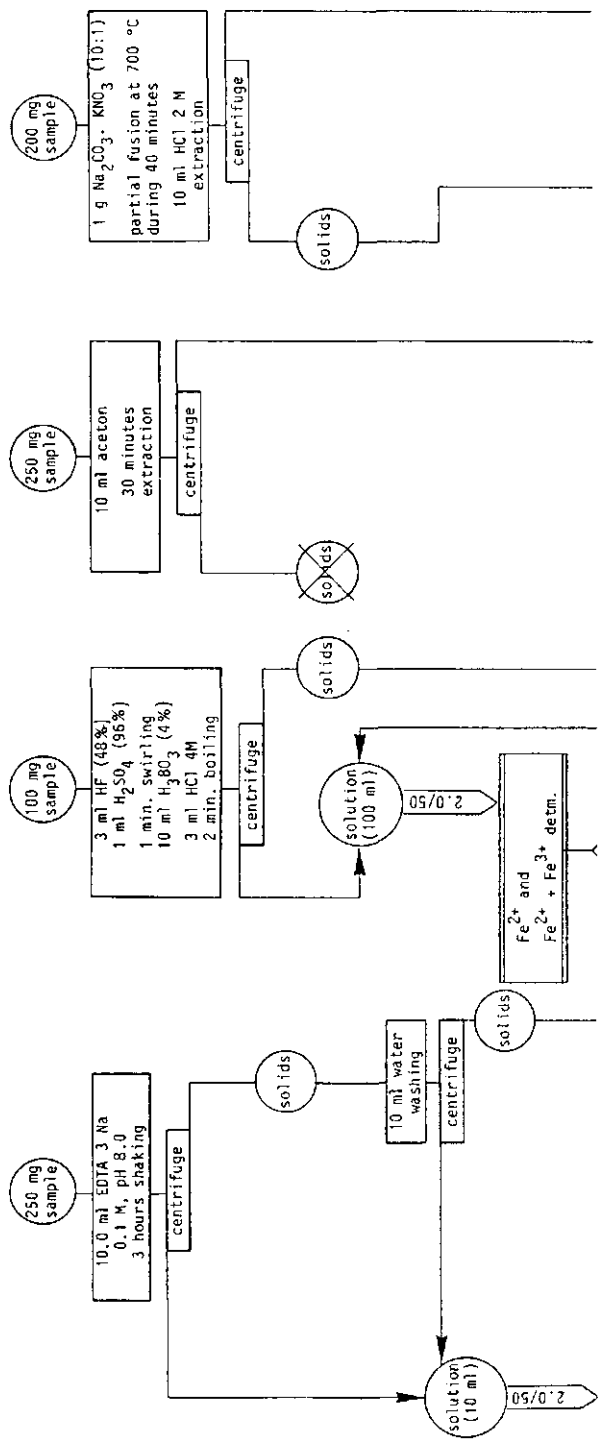
A25: TOTAL SULPHUR

Principle

The sulphur compounds in the soil are converted to sulphate by partial fusion in a mixture of sodium carbonate and potassium nitrate at a temperature of 700° C. Sulphate is measured turbidimetrically with barium as reagent.

Apparatus

Porcelain crucibles of 18 ml (high model)
Muffle furnace
Waterbath
Centrifuge
Spectrophotometer

Reagents

Sodium carbonate (Na_2CO_3)
Potassium nitrate (KNO_3)
Hydrochloric acid 37% (HCl)
Nitric acid 65% (HNO_3)
Phosphoric acid 85% (H_3PO_4)
Acetic acid glacial (CH_3COOH)
Gum arabic
Sodium sulphate (Na_2SO_4)
Barium chloride ($BaCl_2.2H_2O$)
Sodium chloride (NaCl)
Potassium sulphate (K_2SO_4)

> fusion mixture

Thoroughly mix 100 g Na_2CO_3 and 10 g KNO_3.

> 2 M hydrochloric acid

Bring 150 ml distilled water to a 250 ml measuring cylinder. Carefully add 40 ml HCl 37%. Allow to cool. Make up to 250 ml with water and homogenize.

> 25% nitric acid

Bring 150 ml of water to a 250 ml measuring cylinder. Add 90 ml of concentrated HNO_3. Allow to cool and make up to 250 ml with water. Homogenize.

> acetic acid/phosphoric acid mixture

Mix 180 ml acetic acid glacial with 60 ml phosphoric acid 85%.

> gum arabic-acetic acid solution

Weigh 0.5 g gum arabic into a 100 ml measuring cylinder and dissolve in 50 ml of water. Add 50 ml acetic acid glacial and mix thoroughly. Filtrate the solution using a medium hardened filter (e.g. S & S

595½).

0.3% sodium sulphate solution

Dissolve 0.3 g of Na_2SO_4 in 100 ml of water.

barium seed solution

Dissolve 18.0 g of $BaCl_2.2H_2O$ in 44 ml of hot water. Add 1.5 ml of the 0.3% Na_2SO_4 solution. Heat to boiling and cool quickly. Add 4.0 ml of the gum arabic-acetic acid solution. **Prepare this solution just before use.**

1 M sodium chloride

Dissolve 5.8 g NaCl in 100 ml of water.

1000 mg L^{-1} SO_4^{2-} stock solution

Weigh 1.8142 gram potassium sulphate (dried at 105° C) in a 400 ml beaker. Dissolve in about 300 ml distilled water. Transfer the solution to 1 litre volumetric flask. Make up to volume with distilled water and homogenize.

Standard series

Pipette 25 ml of the 1000 mg L^{-1} SO_4^{2-} stock solution into a 50 ml volumetric flask. Make up to volume with water and homogenize. This standard solution is now 500 mg L^{-1} SO_4^{2-}.

Pipette 0, 1, 2, 3, 4 and 5 ml, respectively, of this 500 mg L^{-1} SO_4^{2-} solution as sample in the 50 ml volumetric flask (see measurement). Add 2 ml of 1 M NaCl to each flask. The standard series is now:

Standard 1:   0 mg L^{-1} SO_4^{2-}
Standard 2: 10 mg L^{-1} SO_4^{2-}
Standard 3: 20 mg L^{-1} SO_4^{2-}
Standard 4: 30 mg L^{-1} SO_4^{2-}
Standard 5: 40 mg L^{-1} SO_4^{2-}
Standard 6: 50 mg L^{-1} SO_4^{2-}

Procedure

fusion

Weigh 200 mg (accuracy 0.1 mg) freeze-dried and ground sample into a porcelain crucible. Weigh 1.0 g of the fusion mixture on a weighing paper. Add about 4/5th of the mixture to the crucible. Mix the sample and the fusion mixture thoroughly. Cover this mixture with the remaining (1/5th) fusion mixture. Place the crucible in the muffle furnace and heat to 700°C. Keep at this temperature for exactly 40 min. Remove the crucible from the furnace and allow to cool. Transfer the contents with 10 ml of 2 M HCl to a 50 ml polypropylene centrifuge tube. Place the tube in a boiling waterbath until effervescence of CO_2 stops. Allow to cool and centrifuge for 30 minutes at 3000 rpm. Decant the clear supernatant into a 100 ml volumetric flask. Wash the residue with 25 ml water. Centrifuge again for 30 minutes at 3000 rpm. Decant the

supernatant to the same volumetric flask. Make the flask up to volume with water and homogenize.

Measurement

Pipette the standard series and the NaCl solution (see standard series) or 20 ml of the sample solution into a 50 ml volumetric flask. Make up to about 30 ml with water. Add successively 5.0 ml of the 25% HNO_3 solution and 4 ml of the acetic acid/phosphoric acid mixture. Homogenize. Add 1.00 ml of the barium seed solution and immediately 0.5 g $BaCl_2.2H_2O$. Shake well after each addition and stopper the flask. After 15 minutes shake the flask 5 times and after another 5 minutes another 5 times. Again after 5 minutes add 2.0 ml of the gum arabic-acetic acid solution. Because the timing of the addition of the reagents for the measurement is very critical, the procedure for the measurement should be executed by two persons. Make up to volume with water and homogenize. Leave for 1½ hours. Shake the flask 20 times just before measuring it with a spectrophotometer at a wavelength of 438 nm. If the sample is out of the calibration range, repeat the measurement pipetting less extract (e.g. 10 ml)

Calculation

Prepare a plot of sulphate concentration against absorbance. Read or calculate the sulphate concentration of the sample from this plot.

$$\textit{Total sulphur (mmol kg}^{-1}) = \frac{(C-B) \times mcf \times 52051}{W \times V}$$

$$\textit{Total sulphur (\%)} = \frac{(C-B) \times mcf \times 166.9}{W \times V}$$

where

C   = SO_4^{2-} concentration in sample (mg L^{-1})
B   = SO_4^{2-} concentration in blank (mg L^{-1})
mcf   = moisture correction factor
W   = sample weight (mg)
V   = volume of extract pipetted for measurement (20 ml in standard procedure)
52051 = conversion factor
166.9 = conversion factor

Remarks

-      Use distilled water throughout the procedure.

-      Potassium nitrate is an efficient oxidizing agent and lowers the melting point of the sodium carbonate so that partial fusion occurs without excessive

decomposition of silicates from the soil or the crucible.

- The ratio of the fusion mixture and the temperature are critical. Excess of potassium nitrate leads to temperatures above 700°C. A hard melt is formed and the extraction of sulphate gets very difficult. Moreover, large amounts of silicate are mobilized and may later interfere the assay of sulphate.

- If 20 ml of the extract contains less SO_4^{2-} than the lowest standard of the standard series, pipette also 2 ml of the SO_4^{2-}-standard to the 50 ml volumetric flask (see measurement).

- Take care that all solid barium chloride is dissolved during the mixing of the measuring solution.

- When the extracts are coloured, centrifuge the sample solution after the measurement and measure the clear solution again at the same wavelength. Subtract the absorbance of the clear but coloured solution from the total absorbance.

References

- Begheijn, L.Th., 1980. Methods of Chemical Analysis for Soils and Waters. Department of Soil Science and Geology, Agricultural University Wageningen, 3rd ed., page 32-33.

- Begheijn, L.Th, N. van Breemen and E.J. Velthorst, 1978. Analysis of sulphur compounds in acid sulphate soils and other recent marine soils. Communications in Soil Science and Plant Analysis 9(9):873-882.

A26: ELEMENTARY SULPHUR

Principle

Elementary sulphur is extracted from the soil with acetone. Sulphur is determined turbidimetrically as colloidal sulphur in water.

Apparatus

Shaking machine
Centrifuge
Spectrophotometer

Reagents

Acetone (2-propanone) (C_3H_6O)
Solid sulphur >99.99% (S)

Standard series

Weigh 62.5 mg of solid sulphur into a 250 ml shaking bottle. Add about 150 ml of acetone. Shake until the sulphur has dissolved. Transfer the solution to a 250 ml volumetric flask. Make up to volume with acetone and homogenize. This standard solution is now 250 mg l^{-1} sulphur.
Pipette 0, 1, 2, 3, 4 and 5 ml of this standard solution as sample (see procedure) to a 100 ml volumetric flask. Add also respectively 5, 4, 3, 2, 1 and 0 ml acetone to the volumetric flask. Make up to volume with water and homogenize. The standard series is now:
standard 1:   0.0 mg l^{-1} S
standard 2:   2.5 mg l^{-1} S
standard 3:   5.0 mg l^{-1} S
standard 4:   7.5 mg l^{-1} S
standard 5 10.0 mg l^{-1} S
standard 6: 12.5 mg l^{-1} S

Procedure

Weigh 250 mg (accuracy 0.1 mg) of freeze-dried and ground sample into a 15 ml polypropylene centrifuge tube. Pipette 10 ml acetone to the tube and shake for 30 minutes. Centrifuge for 15 minutes at 3500 rpm.
Pour about 80 ml of water to a 100 ml volumetric flask. Pipette 5 ml of the extract into the flask, while swirling gently. Make up to volume with water and homogenize.

Measurement

After 3 hours measure the absorbance with a spectrophotometer at a wavelength of 420 nm.

Calculation

Prepare a plot of sulphur concentration against absorbance. Read or calculate the sulphur concentration of the sample from this plot.

$$elementary\ sulphur\ (mmol\ kg^{-1}) = \frac{(C-B) \times mcf \times 6237}{W}$$

$$elementary\ sulphur\ (\%) = \frac{(C-B) \times mcf \times 20}{W}$$

where

C	= S concentration in sample (mg l^{-1})
B	= S concentration in blank (mg l^{-1})
mcf	= moisture correction factor
W	= sample weight (mg)
6237	= conversion factor
20	= conversion factor

Remarks

- The standard series is linear from 2.5 to 10.0 mg l^{-1} S.

- If the concentration of the sample is lower than the lowest standard add 0.25 mg solid sulphur to the sample as internal standard.

- High concentrations of organic matter may cause interference by coprecipitation or colouring of the final solution.

References

- Begheijn L.Th., 1980. Methods of Chemical Analysis for Soils and Waters. Department of Soil Science and Geology, Agricutltural University Wageningen, 3rd ed., page 30-31.

- Begheijn L.Th, N. van Breemen and E.J. Velthorst, 1978. Analysis of sulphur compounds in acid sulphate soils and other recent marine soils. Communications in Soil Science and Plant Analysis 9(9):873-882.

A27: NA₃-EDTA-EXTRACTABLE SULPHATES

Principle

Gypsum, non-readily soluble and exchangeable sulphates are extracted by Na_3-E.D.T.A. The sulphate is measured turbidimetrically with barium as reagent.

Apparatus

Shaking machine
Waterbath
Spectrophotometer

Reagents

Ethylenediaminetetraacetic acid trisodium salt (Na_3-EDTA); ($C_{10}H_{13}N_2O_8Na_3.H_2O$)
Hydrochloric acid 37% (HCl)
Nitric acid 65% (HNO_3)
Phosphoric acid 85% (H_3PO_4)
Acetic acid glacial (CH_3COOH)
Gum arabic
Sodium sulphate (Na_2SO_4)
Barium chloride ($BaCl_2.2H_2O$)
Potassium sulphate (K_2SO_4)

0.1 M Na_3-EDTA

Dissolve 18.8 g of Na_3-EDTA in 250 ml distilled water. Transfer to a 500 ml volumetric flask and make up to volume with water. Homogenize.

aqua regia

Mix in a 400 ml beaker 180 ml HCl 37% with 60 ml HNO_3 65%. Cover the beaker with a plastic watchglass (instead of a stopper).

25% nitric acid

Add 150 ml of water to a 250 ml measuring cylinder. Add 90 ml of concentrated HNO_3. Allow to cool and make up to 250 ml with water. Homogenize.

acetic acid/phosphoric acid mixture

Mix 180 ml acetic acid glacial with 60 ml phosphoric acid 85%.

gum arabic-acetic acid solution

Weigh 0.5 g gum arabic into a 100 ml measuring cylinder and dissolve in 50 ml of water. Add 50 ml acetic acid glacial and mix thoroughly. Filtrate the solution using a medium hardened filter (e.g. S & S 595½).

0.3% sodium sulphate solution

Dissolve 0.3 g of Na_2SO_4 in 100 ml of water.

barium seed solution

Dissolve 18.0 g of $BaCl_2.2H_2O$ in 44 ml of hot water. Add 1.5 ml of the 0.3% Na_2SO_4 solution. Heat to boiling and cool quickly. Add 4.0 ml of the gum arabic-acetic acid solution. **Prepare this solution just before use.**

1000 mg L^{-1} SO_4^{2-} stock solution

Weigh 1.8142 gram potassium sulphate (dried at 105° C) in a 400 ml beaker. Dissolve in about 300 ml distilled water. Transfer the solution to a 1 litre volumetric flask. Make up to volume with distilled water and homogenize.

Standard series

Pipette 25 ml of the 1000 mg L^{-1} SO_4^{2-} stock solution into a 50 ml volumetric flask. Make up to volume with water and homogenize. This standard solution is now 500 mg L^{-1} SO_4^{2-}.
Pipette 0, 1, 2, 3, 4, and 5 ml, respectively, of the 500 mg L^{-1} SO_4^{2-}-solution as sample in 50 ml volumetric flasks (see measurement). Continue as described in measurement. The standard series is then:
Standard 1:   0 mg L^{-1} SO_4^{2-}
Standard 2: 10 mg L^{-1} SO_4^{2-}
Standard 3: 20 mg L^{-1} SO_4^{2-}
Standard 4: 30 mg L^{-1} SO_4^{2-}
Standard 5: 40 mg L^{-1} SO_4^{2-}
Standard 6: 50 mg L^{-1} SO_4^{2-}

Procedure

Weigh 250 mg (accuracy 0.1 mg) of freeze-dried and ground sample into a 15 ml polypropylene centrifuge tube. Pipette 10 ml of the Na_3-EDTA solution to the sample. Shake in an end-over-end shaker for 3 hours. Centrifuge for 15 minutes at 3500 rpm. Pipette 2 ml of the clear supernatant into a 25 ml porcelain crucible. Add 2 ml of aqua regia and 1 ml of phosphoric acid 85%. Evaporate on a boiling water bath to constant volume. Add another 2 ml of aqua regia and evaporate again. Add 10 ml of water and warm on the waterbath for a few minutes. Allow to cool for a few minutes. Homogenize the contents of the crucible and transfer it with water to a 50 ml volumetric flask. Make the flask up to volume with water and homogenize.

Measurement

Pipette the standard series or 20 ml of the sample solution into a 50 ml volumetric flask. Make to about 30 ml with water. Add 5.0 ml of the 25% HNO_3 solution. For the samples add 3 ml of acetic acid glacial and for the standard series add 4 ml of the acetic acid/phosphoric acid mixture. Homogenize. Add 1.00 ml of the barium seed solution and immediately 0.5 g $BaCl_2.2H_2O$. Shake well after each addition and stopper

the flask. After 15 minutes, shake the flask 5 times and after another 5 minutes another 5 times. Again after 5 minutes add 2.0 ml of the gum arabic-acetic acid solution. Because the timing of the addition of the reagents of the measurement is very critical, the procedure for the measurement should be executed by two persons. Make up to volume with water and homogenize. Leave for 1½ hours. Shake the flask 20 times just before measuring it with a spectrophotometer at a wavelength of 438 nm. When the sample is out of the calibration range, pipette less sample to the volumetric flask (e.g. 10 ml)

Calculation

Prepare a plot of sulphate concentration against absorbance. Read or calculate the sulphate concentration of the sample from this plot.

$$Na_3\text{-}EDTA \text{ extractable } SO_4^{2-} \text{ } (mmol \text{ } kg^{-1}) = \frac{(C-B) \times mcf \times 26025}{W \times V}$$

where

C $= SO_4^{2-}$ concentration in sample (mg L^{-1})
B $= SO_4^{2-}$ concentration in blank (mg L^{-1})
mcf   = moisture correction factor
W   = sample weight (mg)
V   = volume of extract pipetted for measurement (standard 20 ml)
26025 = conversion factor

Remarks

-       After washing with water, the residue may be used for further extraction of jarosite in the soil (see figure 9).

-       Use distilled water throughout the procedure.

-       Because of the use of concentrated acids, follow the safety precautions.

-       If 20 ml of the extract contains less SO_4^{2-} than the lowest standard of the standard series, pipette also 2 ml of the SO_4^{2-}-standard to the 50 ml volumetric flask (see measurement).

-       When the extracts are coloured, centrifuge the sample solution after the measurement and measure the clear solution again at the same wavelength. Subtract the absorbance of the clear solution from the total absorbance.

-       Take care that all solid barium chloride is dissolved during the mixing of the measuring solution.

References

- Begheijn, L.Th., 1980. Methods of Chemical Analysis for Soils and Waters. Department of Soil Science and Geology, Agricultural University Wageningen, 3rd ed., page 25-26 .

- Begheijn, L.Th., N. van Breemen and E.J. Velthorst, 1978. Analysis of sulphur compounds in acid sulphate soils and other recent marine soils. Communications in Soil Science and Plant Analysis 9(9):873-882.

A28: JAROSITE

Principle

After removal of the Na_3-EDTA-extractable sulphates, jarosite $[KFe_3(SO_4)_2(OH)_6]$ is dissolved in hot hydrochloric acid. The sulphate is determined turbidimetrically with barium as reagent.

Apparatus

Centrifuge
Waterbath
Spectrophotometer

Reagents

Hydrochloric acid 37% (HCl)
Nitric acid 65% (HNO_3)
Phosphoric acid 85% (H_3PO_4)
Acetic acid glacial (CH_3COOH)
Gum arabic
Sodium sulphate (Na_2SO_4)
Barium chloride ($BaCl_2.2H_2O$)
Potassium sulphate (K_2SO_4)

    4 M hydrochloric acid

Bring 150 ml of distilled water to a measuring cylinder of 250 ml. Carefully add 80 ml HCl 37%. Allow to cool. Make up to 250 ml with water and homogenize.

    aqua regia

Mix 180 ml HCl 37% with 60 ml HNO_3 65% in a 400 ml beaker. Cover the beaker with a plastic watchglass (instead of a stopper).

    25% nitric acid

Bring 150 ml of water to a 250 ml measuring cylinder. Add 90 ml of concentrated HNO_3. Allow to cool and make up to 250 ml with water. Homogenize.

    acetic acid/phosphoric acid mixture

Mix 180 ml acetic acid glacial with 60 ml phosphoric acid 85%.

gum arabic-acetic acid solution

Weigh 0.5 g gum arabic into a 100 ml measuring cylinder and dissolve it in 50 ml of water. Add 50 ml acetic acid glacial and mix thoroughly. Filtrate the solution using a medium hardened filter (e.g. S & S 595½).

0.3% sodium sulphate solution

Dissolve 0.3 g of Na_2SO_4 in 100 ml of water.

barium seed solution

Dissolve 18.0 g of $BaCl_2.2H_2O$ in 44 ml of hot water. Add 1.5 ml of the 0.3% Na_2SO_4 solution. Heat to boiling and cool quickly. Add 4.0 ml of the gum arabic-acetic acid solution. **Prepare this solution just before use.**

1000 mg L^{-1} SO_4^{2-} stock solution

Weigh 1.8142 gram potassium sulphate (dried at 105° C) in a 400 ml beaker. Dissolve in about 300 ml distilled water. Transfer the solution to a 1 litre volumetric flask. Make up to volume with distilled water and homogenize.

Standard series

Pipette 25 ml of the 1000 mg L^{-1} SO_4^{2-} stock solution into a 50 ml volumetric flask. Make up to volume with water and homogenize. This standard solution is now 500 mg L^{-1} SO_4^{2-}.

Pipette respectively 0, 1, 2, 3, 4, and 5 ml of this 500 mg L^{-1} SO_4^{2-} solution as sample in 50 ml volumetric flasks (see measurement). Continue as described in measurement. The standard series is then:
Standard 1:   0 mg L^{-1} SO_4^{2-}
Standard 2: 10 mg L^{-1} SO_4^{2-}
Standard 3: 20 mg L^{-1} SO_4^{2-}
Standard 4: 30 mg L^{-1} SO_4^{2-}
Standard 5: 40 mg L^{-1} SO_4^{2-}
Standard 6: 50 mg L^{-1} SO_4^{2-}

Procedure

Decant the rest of the supernatant of the NA_3-EDTA soluble sulphates **(see chapter 25)** and wash the residue with 10 ml of water. Centrifuge for 10 minutes at 3000 rpm. Decant the supernatant. Transfer the residue with 10 ml of 4 M HCl to a 50 ml beaker. Cover the beaker with a watch glass and place it on a boiling waterbath for about 2 hours. Allow to cool and transfer the contents to a 50 ml polypropylene centrifuge tube. Centrifuge for 15 minutes at 3000 rpm. Decant the supernatant into a 50 ml volumetric flask. Wash with 10 ml of water. Centrifuge again for 15 minutes at 3000 rpm. Decant the supernatant to the same volumetric flask. Make the flask up to volume with water and homogenize.

Pipette 10 ml of the extract into a 50 ml porcelain dish. Add 2 ml of aqua regia and next 1 ml of phosphoric acid (85%). Evaporate on a boiling waterbath to constant volume. Add another 2 ml of aqua regia and evaporate again. Add 10 ml of water and warm for a few minutes. Allow to cool for a few minutes. Homogenize the contents of the crucible and transfer it with water to a 50 ml volumetric flask. Make the flask up to volume with water and homogenize.

Measurement

Pipette the standard series (see above) or 20 ml of sample solution into a 50 ml volumetric flask. Make to about 30 ml with water. Add 5.0 ml of the 25% HNO_3 solution. For the samples add 3 ml acetic acid glacial and for the standard series add 4 ml of the acetic acid/phosphoric acid mixture. Homogenize. Add 1.00 ml of the barium seed solution and immediately 0.5 g $BaCl_2.2H_2O$. Shake well after each addition and stopper the flask. After 15 minutes shake the flask 5 times and after another 5 minutes another 5 times. Again after 5 minutes add 2.0 ml of the gum arabic-acetic acid solution. Because the timing of the addition of the reagents for the measurement is very critical, the procedure for the measurement should be done by two persons.

Make up to volume with water and homogenize. Leave for 1½ hours. Shake the flask 20 times just before measuring it with a spectrophotometer at a wavelength of 438 nm. If the sample is out of the calibration range, repeat the measurement, pipetting less extract (e.g. 10 ml)

Calculation

Prepare a plot of sulphate concentration against absorbance. Read or calculate the sulphate concentration of the sample from this plot.

$$Jarosite \ (mmol \ kg^{-1}) = \frac{(C-B) \times mcf \times 26025}{W \times V}$$

where

C	= SO_4^{2-} concentration in sample (mg L^{-1})
B	= SO_4^{2-} concentration in blank (mg L^{-1})
mcf	= moisture correction factor
W	= sample weight (mg)
V	= volume of extract pipetted for measurement (standard 20 ml)
25025	= conversion factor

Remarks

- The residue may be used for pyrite extraction in the soil (see figure 9).

- Use distilled water throughout the procedure.

- Because of the use of concentrated acids, follow the safety precautions.

- If 20 ml of the extract contains less SO_4^{2-} than the lowest standard of the standard series, pipette also 2 ml of the SO_4^{2-}-standard to the 50 ml volumetric flask (see measurement).

- Take care that all solid barium chloride is dissolved during mixing of the measuring solution.

- When the extracts are coloured centrifuge the sample solution after the measurement and measure the clear solution again at the same wavelength. Subtract the absorbance of the clear solution from the total absorbance.

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A29: PYRITE

Principle

Pyrite (FeS$_2$) is dissolved with nitric acid. In case non-pyritic iron (iron (II) and iron (III)) have been removed, iron may be determined with A.A.S. In case Na$_3$-EDTA-extractable sulphates and jarosite have been removed, sulphate may be determined turbidimetrically with barium as reagent. Choose one of the methods and select the appropriate procedure for measurement.

Apparatus

Freeze-drying machine
Waterbath
Diluter
A.A.S.
Spectrophotometer

Reagents

Nitric acid 65% (HNO$_3$)
Hydrochloric acid 37% (HCl)
Phosphoric acid 85% (H$_3$PO$_4$)
Sodium hydroxide (NaOH)
Acetic acid glacial (CH$_3$COOH)
Gum arabic
Sodium sulphate (Na$_2$SO$_4$)
Barium chloride (BaCl$_2$.2H$_2$O)
Sodium chloride (NaCl)
Ampoule for 1000 mg L^{-1} Fe
Potassium Sulphate (K$_2$SO$_4$)

4 M hydrochloric acid

Bring 150 ml of distilled water to a measuring cylinder of 250 ml. Carefully add 80 ml HCl 37%. Allow to cool. Make up to 250 ml with water and homogenize.

0.2 M hydrochloric acid

Dilute 25 ml 4 M HCl to 500 ml with water.

1 M NaOH

Dissolve 20 g NaOH in 500 ml of water.

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1 M NaCl

Dissolve 29 g NaCl in 500 ml of water.

25% nitric acid

Add 150 ml of water to a 250 ml measuring cylinder. Add 90 ml of concentrated HNO_3. Allow to cool and make up to 250 ml with water. Homogenize.

acetic acid/phosphoric acid mixture

Mix 180 ml acetic acid glacial with 60 ml phosphoric acid 85%.

gum arabic-acetic acid solution

Weigh 0.5 g gum arabic into a 100 ml measuring cylinder and dissolve it in 50 ml of water. Add 50 ml acetic acid glacial and mix thoroughly. Filtrate the solution using a medium hardened filter (e.g. S & S 595½).

0.3% sodium sulphate solution

Dissolve 0.3 g of Na_2SO_4 in 100 ml of water.

barium seed solution

Dissolve 18.0 g of $BaCl_2.2H_2O$ in 44 ml of hot water. Add 1.5 ml of the 0.3% Na_2SO_4 solution. Heat to boiling and cool quickly. Add 4.0 ml of the gum arabic-acetic acid solution. **Prepare this solution just before use.**

1000 mg L^{-1} Fe stock solution

Dilute the ampoule according to the manufacturer's instructions.

1000 mg L^{-1} sulphate stock solution

Weigh 1.8142 gram potassium sulphate (dried at 105° C) in a 400 ml beaker. Dissolve in about 300 ml distilled water. Transfer the solution to a 1 litre volumetric flask. Make up to volume with distilled water and homogenize.

dilution solution for Fe measurement

Dissolve 5 g sodium chloride in 400 ml water. Add 25 ml of the 4 M HCl solution and make total volume to 500 ml with water. This solution is now 1% NaCl and 0.2 M HCl.

Standard series

<u>Fe</u>

Pipette 10 ml of the 1000 mg L^{-1} Fe stock solution into a 100 ml volumetric flask. Make up to volume with water and homogenize. This standard solution is now 100 mg L^{-1} Fe.
Pipette 0, 5, 15 and 25 ml of the 100 mg L^{-1} Fe solution to 100 ml volumetric flasks.

Add 2.5 ml of the 4 M HCl solution to each flask. Make each flask up to volume with water and homogenize. The standard series is now:
Standard 1:   0.0 mg L^{-1} Fe
Standard 2:   5.0 mg L^{-1} Fe
Standard 3: 15.0 mg L^{-1} Fe
Standard 4: 25.0 mg L^{-1} Fe

SO_4^{2-}

Pipette 25 ml of the 1000 mg L^{-1} SO_4^{2-} stock solution into a 50 ml volumetric flask. Make up to volume with water and homogenize. This standard solution is now 500 mg L^{-1} SO_4^{2-}.
Pipette respectively 0, 1, 2, 3, 4 and 5 ml of this 500 mg L^{-1} SO_4^{2-} solution as sample in 50 ml volumetric flasks (see measurement). Add 2 ml of 1 M NaCl. Continue as described in measurement. The standard series is then:
Standard 1:   0 mg L^{-1} SO_4^{2-}
Standard 2: 10 mg L^{-1} SO_4^{2-}
Standard 3: 20 mg L^{-1} SO_4^{2-}
Standard 4: 30 mg L^{-1} SO_4^{2-}
Standard 5: 40 mg L^{-1} SO_4^{2-}
Standard 6: 50 mg L^{-1} SO_4^{2-}

Procedure

Freeze-dry the washed residue of the jarosite extraction **(see chapter 26)** or of the iron (II) and iron (III) extraction (see **chapter 19)**.
Transfer the residue with 10 ml nitric acid 70% into a 50 ml porcelain dish. Evaporate the acid on a boiling waterbath. Extract the residue with 5 ml of 4 M HCl. Warm for 5 minutes on a waterbath. Transfer the contents to a 50 ml polypropylene centrifuge tube. Centrifuge for 15 minutes at 3000 rpm. Decant the clear supernatant into a 100 ml volumetric flask. Wash the residue in the centrifuge tube with 10 ml of water and centrifuge again for 15 minutes at 3000 rpm. Decant the supernatant in the same volumetric flask. Make up to volume with water and homogenize.

Measurement

iron

Dilute the sample 1:1 with the dilution solution. Use A.A.S. to measure Fe. The wavelength is 248.3 nm and the flame is an air/acetylene flame. If the sample is out of the calibration range dilute the sample but make sure that the background is 0.5% NaCl and 0.1 M HCl.

sulphate

Pipette the standard series (see above) or 20 ml of the sample solution into a 50 ml

volumetric flask. Add 2 ml 1 M NaCl to the standard series and 2 ml 1 M NaOH to the samples. Make up to about 30 ml with water. Add successively 5.0 ml of the 25% HNO_3 solution and 4 ml of the acetic acid/phosphoric acid mixture. Homogenize. Add 1.00 ml of the barium seed solution and immediately 0.5 g $BaCl_2.2H_2O$. Shake well after each addition and stopper the flask. After 15 minutes shake the flask 5 times and after another 5 minutes another 5 times. Again after 5 minutes add 2.0 ml of the gum arabic-acetic acid solution. Because the timing of the addition of the reagents at the SO_4^{2-}-measurement is very critical, the procedure for the measurement should be executed by two persons.

Make up to volume with water and homogenize. Leave for 1½ hours. Shake the flask 20 times just before measuring it with a spectrophotometer at a wavelength of 438 nm. If the sample is out of the calibration range, repeat the measurement pipetting less extract (e.g. 10 ml)

Calculation

<u>Fe</u>

$$Pyrite\ (mmol\ kg^{-1}) = \frac{(C-B) \times D \times mcf \times 1791}{W}$$

where

C   = Fe concentration in sample (mg L^{-1})
B   = Fe concentration in blank (mg L^{-1})
D   = dilution factor (standard is 2)
mcf = moisture correction factor
W   = sample weight (mg)
1791 = conversion factor

<u>SO_4^{2-}</u>

Prepare a plot of sulphate concentration against absorbance. Read or calculate the sulphate concentration of the sample from this plot.

$$Pyrite\ (mmol\ kg^{-1}) = \frac{(C-B) \times mcf \times 52051}{W \times V}$$

where

C   = SO_4^{2-} concentration in sample (mg L^{-1})
B   = SO_4^{2-} concentration in blank (mg L^{-1})

mcf = moisture correction factor
W = sample weight (mg)
V = volume of extract pipetted for measurement (standard 20 ml)
52051 = conversion factor

Remarks

- Use distilled water throughout the procedure.

- Because of the use of concentrated acids, follow the safety precautions.

- Iron may also be measured colorimetrically by o-phenanthroline.

- If 20 ml of extract contains less SO_4^{2-} than the lowest standard in the standard series, pipette 2 ml of the SO_4^{2-}-standard.

- Take care that all solid barium chloride is dissolved during the mixing of the measuring solution.

- When the extracts are coloured, centrifuge the sample solution after the measurement and measure the clear solution again at the same wavelength. Subtract the absorbance of the clear solution from the total absorbance.

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Section B

WATER ANALYSIS

by E.J. Velthorst

B01: COLLECTION and PRESERVATION of WATER SAMPLES

Introduction

The most common kinds of water samples which are monitored and sampled are rain, throughfall, pool, pool soil water, and soil water samples. Sampling means to collect a portion of material small enough in volume to be conveniently transported to, and handled in the laboratory, and representative for the bulk. To collect a water sample correctly is not an easy task. No general procedures can be given, because of the complexity of the sample itself.

The sample is usually removed from its environment. This implies that the concentration of the components must be the same in the sample as in the total environment. This is not as easy as it sounds. Field workers, who usually collect the field samples, usually have an attitude which differs markedly from that of an analyst. Because it flows and mixes easily, water is usually considered as much more homogeneous than soil itself. In many cases, this is far from the truth, and the amount and composition of water samples varies strongly with small changes in location. Sometimes representative samples can only be obtained by making composites of samples that have been collected over a period of time or at different sampling points.

In addition, samples must be collected in such a way that no significant changes occur between collection and analysis. In the following paragraphs we will address some of these problems.

General notes

The choice of a sample location not only depends on the purpose of the investigation, but also on local conditions, depth, and the frequency of sampling. The details of collection vary so much with local conditions that no specific recommendations are applicable. A critical point is to insure that the sample is representative of the actual composition of the whole. Considerable errors are likely with **small amounts** of sample. In such cases it is more informative to analyze numerous separate samples instead of one composite.

Sample collection is a delicate and precise job. A sample should remain the same as it was in the field, and without changes or contamination when it reaches the laboratory. This sample handling step has to be done very accurately. Therefore it is important that persons in charge of sampling are instructed precisely or even have an analytical background in order to ensure proper sampling. Reliable results will only be obtained, if the sampling procedure is executed satisfactorily. This means: proper preparation in the laboratory before sampling, accurate field work and, finally, proper handling and cleaning when entering the laboratory.

Start by rinsing a sample bottle in the laboratory with HCl (2 M), distilled water (at least three times) and drying. Drying is a risky step in relation to interferences. Sometimes it's better to stopper and rinse the bottle various times with sample water before sampling. On the sample location, rinse three times with sample water

before sampling. Fill a sample bottle completely and fill the screwcap too. Execute this work with analytical precision and cleanliness. Don't touch the inner part of the sample bottle, screwcap or even the water sample itself.

Throughfall and rain water funnels are cleaned with a brush and distilled water and allowed to stand for 5 minutes to drain. Connect the funnel to a clean bottle. Clean the used bottle in the laboratory with a brush and distilled water and dry. Sometimes, samples can only be obtained by making composites of samples that have been collected over a longer period of time. In that case, collect the different quantities and prepare a sample by adding together *proportional* quantities of the collected volumes.

Another important aspect is the choice of the *sample bottles*. Not only the kind of the bottle (adsorption, desorption), but also the bottle volume influences the analytical results. Small amounts of sample volume have considerable contact with large bottles and less contact with small bottles. In spite of careful pre-cleaning, sample bottles are still a major source of errors. Polythene bottles, for instance, increase the chlorine content with time or adsorb organic material. Errors increase with the permeability of the bottle wall. Glass bottles release sodium and silicon with time. Therefore, it depends on the elements to analyse, which kind of sample bottle is needed. A general solution is not available. Sample bottles should be properly marked and recorded, preferably on the sample location.

Ceramic cups have to be treated with HCl (0.1 M) and distilled water before installing in the field. Cups possess a small cation exchange capacity (CEC). Moreover, aluminium and silica are released from the cup. Acid washing results in proton occupying the exchange sites. The reactivity is minimized with cleaning. Sorption of dissolved organic carbon by ceramic cups is known: 20-30% of DOC is absorbed by new cups. If sorption sites are occupied, dissolved organic carbon will percolate through the cups without qualitative or quantitative changes, even at low DOC concentrations. Therefore it is important to suction the cups repeatedly in the field before use as samplers. After installation, cups should be suctioned weekly for two or three months, before they are used as a sampler.

Sampling watersamples for *trace elements* is extremely difficult. It is almost impossible to avoid serious errors. One of the major problems with trace elements is pollution. Even the most pure quality chemicals and water can't prevent that even in dust-free laboratories, pollution is the most important error. As soon as a pre-cleaned sample bottle is leaving the conditioned environment, pollution starts. Because of low natural concentrations, these errors are considerable, and often proper analytical result cannot be obtained. Therefore, trace element analyses of water obtained from the field should be handled with great care.

Algae and bacteria influence the concentration of a number of elements. Bacteria are responsible for changing NO_3 and NH_4 contents of water samples. No additives are known which do not change the composition of the sample.

water from undisturbed soil only. The pit is next filled with soil material again.

The injection needle is connected to a 250 ml glass bottle with screwcap and vacuum septum at 50 hPa suction. The water around the cup will be sucked into the cup, the tube and the glass bottle. In the laboratory new cups are normally checked for leakage, slowly flushed (suction) with 1 litre HCl (0.1 M) and distilled water. In this way the cup is cleaned and contamination of the samples by cup material is avoided. After installation in the sample pit, weekly suction for more than 2 months is necessary before the real sampling starts. At least 300 ml soil water has to be suctioned to reach equilibrium.

The porous ceramic plate used for samples from near the surface is made of a pvc bottom plate (diameter 17 cm), containing a sink hole. The sink hole is connected (glued) with teflon tubing provided with an injection needle. The hole is covered with a porous ceramic plate (porcelain P80). On the edge of the ceramic plate a pvc ring is glued. The porous ceramic plate is carefully installed between the upper soil layer and the litter layer. A glass bottle (250 ml, 50 hPa suction) is connected to the needle and water sample above the plate is obtained. Vacuum bottles (50 hPa suction) are replaced every time new samples are collected.

For sampling *pool soil water,* a pvc plate is provided with small horizontal sloping sink holes at different heights (figure 12). These holes are covered with inert porous netting. The holes are separated from each other and on both sides connected with a teflon tubing (connected to an injection needle) which reaches the surface of the pool water. The pvc plate is installed into the pool soil and the holes are filled with gas free water. The teflon tube is stoppered under the surface (not on the bottom to prevent turbidity) of the pool water. The system is left for a few weeks to obtain an equilibrium with the water in the soil of the pool. A sample is collected by carefully raising the tube above the water surface and carefully pressing nitrogen gas on one side and collecting the water sample from the other side of the tube. Sample pH is measured immediately.

To prevent oxidation of sulphides, a subsample is injected into a small (30 ml) glass bottle provided with a rubber septum and filled with nitrogen gas and zinc acetate. To prevent iron oxidation the sample is acidified to pH=2 with HCl (1 M). Sulphate and carbon should be analyzed on the day of sampling. The system is again filled with gas free water. To prevent contamination, sampling starts with the upper depth. Samples collected from pool water should be taken in the middle of that pool and at mid depth to get a representative sample for that pool. If possible, collect a sample from top to bottom in the middle of the pool. Depth, pool flow and distance from shore and from one shore to another influences the sample composition.

Sea water spray (cyclic salt) often gives higher contents of NaCl and $MgCl_2$, and correction for these elements are sometimes necessary.

Figure 12. Sampling pool water
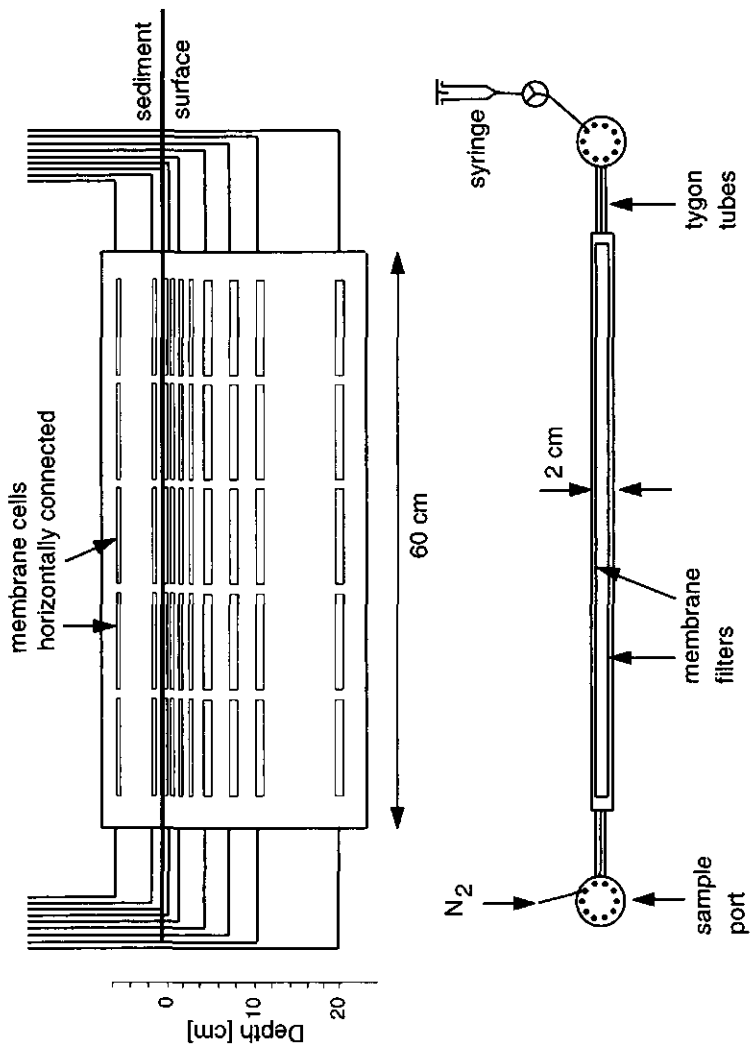
Preservation

To prevent significant changes during transport, special precautions should be taken. For example a sample can be transported in a cool box to minimize biodegradation or volatization between sampling and analysis time. Avoid freezing because glass containers may break. Freezing also may influence the pH and separate dissolved organic matter from the water phase. Keep samples cool in a refrigerator at 4° C. Mercury or chloroform may be needed to prevent growth of micro-organisms. Microbiologial activity may be responsible for changes in the nitrate and ammonium content or for reduction of sulphate to sulphide and chlorine to chloride. Fe^{2+} may be lost from solution through oxidation and precipitation and phosphate and nitrogen concentration may change. One should be very careful with mercury in field experiments, because it causes environmental damage. Use chemical preservatives only when they do not interfere with the required analyses.

Suspended material in samples is another source of error. Filtration over a 0.45 µm filter is usually accepted to distinguish between dissolved and suspended material. In general however, *any* amount of suspended material should be separated by decantation, centrifugation or filtration. These steps introduce errors. Filters for example contain NH_4^+. On the other hand, substantial errors are induced by the interaction between dissolved and suspended material. If necessary, split up the sample and preserve separately.

Adsorption or ion exchange with the wall of the sample container may influence some cations (e.g. Al, Fe and Mn). Preserve the samples for analysis of these cations in separate bottles and acidify to pH 2. The pH varies significantly with changes in temperature, precipitation, redox potential etc. Calcium may decrease, due to precipitation of calcium carbonate; iron and manganese are soluble in lower oxidation state, but insoluble in higher oxidation state (redox potential). Silica and sodium may be liberated from glass, but not from plastic. Avoid losses of volatile materials by collecting samples in a completely filled container.

The sampling period itself causes errors. Periods between sample collection are often a fortnight or even longer. Nitrate and ammonium concentrations may change dramatically during such a period. So the sample offered to the laboratory is probably not very different from that in the field at the moment of sampling, but major sample changes may have taken place during the period in the collector. Attention should be given to that problem. Sometimes it is better to measure components on the sample site or even in a sample pit. Disadvantage is the changing weather conditions during the seasons (frost, rain, etc.). This certainly influences the obtained (field) results. Measurements in the laboratory don't have this problem.

Laboratory

After entering the laboratory pH (if not possible in the field), conductivity, total and inorganic carbon of the samples should be measured as soon as possible, because optimal preservation is impossible. Sample filtration before analysis already causes insuperable errors. After measurement of pH, Ec, and carbon, samples have to be filtered. A membrane filter (0.45 µm) is used and the sample is split up in 2 portions. One portion is acidified to pH 2 for cation analysis and the other is used for anion analysis. Ammonium, nitrate and sulphate analyses should be carried out as soon as possible.

Remarks

- The suction in the vacuum glass bottles can be varied. Low suction gives less water, high suction may give unwanted sample water. Ideally, the suction force should be similar to the prevalent suction forces in the soil.

- Soil water and pool soil water are already filtered by the ceramic cup and netting. Still these samples need to be checked. Pool soil water very easily shows precipitation.

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B02. WATER ANALYSIS PROCEDURE

The following is a very brief outline of the sequence of analyses as they should be carried out on natural water samples. In our laboratory, we do not study soil pollution, and therefore only major elements and components are analyzed.

Procedure

- Open the sample flask and measure pH and conductivity immediately.
- If carbonate or hydrogencarbonate are requested, pipette 50.0 mls of sample and titrate directly.
- If inorganic and total carbon are requested, measure these elements as soon as possible.
- Filter part of the sample over a 0.45 μm millipore filter and use this filtered sample for determination of Cl^-, NO_3^- and SO_4^{2-}.
- Split the sample and add to one part HCl (1 M) to pH 3-4. Homogenize and keep in a refrigerator.
- Determine NH_4^+ and $H_2PO_4^-$ in the acidified sample.
- Determine H_4SiO_4, Al^{3+}, Ca^{2+}, Mg^{2+}, Na^+, K^+, Fe^{2+} and Mn^{2+} in the acidified sample. To measure monomeric Al^{3+}, allow the acidified sample to stand for at least 24 hours.
- Complete the ionic balance using CO_3^{2-}/HCO_3^-, inorganic and total carbon to calculate S.O.A. (sum organic anions).
- Calculate the sum of all cations and all anions. If the difference between sum cations and sum anions is more than 5%, check all the analyses.
  Check the synthetic (artificial) watersamples. If possible, repeat analysis of one or more elements. Be aware that the measurement of pH, Ec, CO_3^{2-}, HCO_3^-, inorganic carbon, total carbon, NH_4^+, $H_2PO_4^-$, NO_3^- and SO_4^{2-} cannot be repeated.

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B03: SYNTHETIC REFERENCE SAMPLES

Introduction

One way to check the quality of a measurement is by frequently analyzing a synthetic sample of known composition. This synthetic sample should have more or less the same composition as the unknown sample. Another way is to use natural watersamples which have been analyzed a number of times and are used for the same purpose. By analyzing these samples a (quality) check of the determination can be obtained. Disadvantage of natural watersamples is their short tenability. Therefore artificial water samples are preferred.

Types of reference samples

Mainly soil, rain and throughfall water samples are analyzed. Rain water is collected with rain gauges. Throughfall water is water leaking through leaves and needlecanopy of a forest. Water from the soil is obtained by means of ceramic suction cups or plates, that are installed in the soil at different depths. For each type of sample a reference sample is prepared. Its composition is based on mean concentrations of rain water, throughfall water and soil water.

Composition of synthetic reference samples

------------------Composition in $mmol_c.m^{-3}$------------------

	Rain water	Throughfall water	Soil water
Na	70	225	300
K	5	175	175
Ca	40	125	500
Mg	30	75	300
NH_4	140	850	85
H	40	<10	50-100
Al	0	0	1000
F	4	20	25
Cl	85	200	225
NO_3	75	200	1300
SO_4	160	750	1000
HCO_3	0	200	100
H_2PO_4	1	5	2
H_4SiO_4	0	0	500

Apparatus

Balance (0.001 mg).
Gas cylinder (pure CO_2).
Ultra pure water (milli-Q).

Chemicals used for synthetic reference samples

	mol mass. in $kg.mol^{-1}$	
NaCl p.a.	0.05844	
NaF p.a.	0.04199	
$NaHCO_3$ p.a.	0.08401	
KCL p.a.	0.07456	
KNO_3 p.a.	0.10111	
K_2SO_4 p.a.	0.17427	
KH_2PO_4 p.a.	0.13609	
NH_4Cl p.a.	0.05349	
NH_4HCO_3 p.a.	0.07906	
$(NH_4)_2SO_4$ p.a.	0.13214	
$CaCO_3$ p.a.	0.10009	
$MgSO_4.7H_2O$ p.a.	0.24648	
$Al(NO_3)_3.9H_2O$ p.a.	0.37513	
$SiO_2.nH_2O$ p.a.		
HCl 0.1 M p.a.		0.0987 mol(+)$.L^{-1}$
HNO_3 0.2 M p.a.		0.2014 mol(+)$.L^{-1}$
H_2SO_4 0.1 M p.a.		0.1983 mol(+)$.L^{-1}$

Reagents

To prepare reference samples, ultra pure chemicals are used. All chemicals with exception of $(NH_4)HCO_3$, $NaHCO_3$ and $Al(NO_3)_3.9H_2O$ are dried at 105°C and kept in a desiccator. $MgSO_4$ is prepared by heating of $MgSO_4.7H_2O$ at 700°C for a few hours. All chemicals are weighed directly after heating. Acids, such as HCl, H_2SO_4 and HNO_3, are prepared from ampoules. Freshly prepared, ultra pure water is used to make solutions and dilutions. Silica is weighed in hydrated form and corrected for the water content by determining loss on ignition. For proper weighing and storage stock solution concentrations are ten times higher than those of synthetic samples.

Preparation of the rain water stock solution

First pipette HCl and HNO_3 into a 1 litre beaker. Dissolve $CaCO_3$ in this acid mixture and

boil gently for several minutes to remove CO_2. Fill the beaker to approximately 800 ml with ultra pure water. Add while stirring $(NH_4)_2SO_4$, NaCl, $MgSO_4$, KCl, NaF, KH_2PO_4 and $Al(NO_3)_3.9H_2O$. Before adding the next salt, wait until the previous one has been totally dissolved. Cool and transfer to a 1 litre volumetric flask. Make up with ultra pure water and homogenize. Transfer to a bottle. Add 0.5 ml chloroform to preserve the solution. Keep in the refrigerator.

Composition of the rain water stock solution.

Reagent	Weight mg	mls	$mmol_c.m^{-3}$
$(NH_4)_2SO_4$	92.5		1400
NaCl	38.6		660
$CaCO_3$	20.0		Ca 400
$MgSO_4$	18.0		300
KCl	3.7		50
NaF	1.7		40
KH_2PO_4	1.4		10
$Al(NO_3)_3.9H_2O$	93.8		750
HNO_3		3.50	NO_3 705
HCl		1.00	Cl 99
			H 404

Rain water working solution

Pipette 10.0 ml stock solution into a 100 ml volumetric flask. Make up with distilled water and homogenize.

Concentration of the rain water working solution.

	$mmol_c/m^{-3}$		
Na	70	F	4
K	6	Cl	81
Ca	40	NO_3	145
Mg	30	SO_4	170
NH_4	140	H_2PO_4	1
H	40		
Al	75		
$\Sigma+$	401	$\Sigma-$	401

Preparation of the throughfall stock solution

First pipette H_2SO_4 into a 1 litre beaker containing 200 ml distilled water. Dissolve $CaCO_3$ and boil gently for a few minutes to remove CO_2. Add approximately 600 ml distilled water. Add, while stirring, $(NH_4)SO_4$, KNO_3, $NaHCO_3$, $(NH_4)HCO_3$, NaCl, NH_4Cl, $MgSO_4$, NaF and KH_2PO_4. Before adding the next salt, wait until the previous one has been totally dissolved. Cool. Transfer to a 1 litre volumetric flask. Make up to volume with ultra pure water and homogenize. Transfer to a bottle and add 0.5 ml chloroform to preserve the solution. Keep in a refrigerator.

Composition of the throughfall stock solution.

Reagent	Weight mg	mls	$mmol_c.m^{-3}$
$(NH_4)_2SO_4$	429.5		6500
KNO_3	202.2		2000
$NaHCO_3$	84.0		1000
NH_4HCO_3	79.1		1001
$CaCO_3$	60.1		Ca 1200
NaCl	58.6		1001
NH_4Cl	53.5		1000
$MgSO_4$	45.1		750
NaF	8.4		200
KH_2PO_4	6.8		50
H_2SO_4	10.0		H 783
			SO_4 1983

Throughfall working solution

Pipette 10.0 ml stock solution into a 100 ml volumetric flask. Make up with distilled water and homogenize.

Concentrations of the throughfall working solution.

--------------------------------$mmol_c.m^{-3}$-----------------------------------

Na	220	F	20
K	205	Cl	200
Ca	120	NO_3	200
Mg	75	SO_4	923
NH_4	850	HCO_3	200
H	78	H_2PO_4	5
$\Sigma+$	1548	$\Sigma-$	1548

Preparation of the soil water stock solution

First pipette H_2SO_4 into a 1 litre beaker, containing 200 ml distilled water. Dissolve $CaCO_3$. Boil gently for a few minutes to remove CO_2. Add approximately 600 ml distilled water. Add, while stirring, $Al(NO_3)_3.9H_2O$, $MgSO_4$, KNO_3, NaCl, $(NH_4)HCO_3$, $NaHCO_3$, NaF and KH_2PO_4. Before adding the next salt, wait until the previous one has been totally dissolved. Cool. Transfer to a 1 litre volumetric flask. Make up to volume with ultra pure water and homogenize. Transfer to a 1 litre bottle. Add 0.5 ml chloroform to preserve the solution.

Composition of the soil water stock solution.

Reagent	Weight mg	mls	$mmol_c.m^{-3}$
$Al(NO_3)_3.9H_2O$	1250.4		10000
$CaCO_3$	250.2		Ca 5000
$MgSO_4$	180.5		3000
KNO_3	176.9		1750
NaCl	131.5		2250
NH_4HCO_3	59.3		750
$NaHCO_3$	21.0		250
NaF	10.5		250
KH_2PO_4	2.7		20
H_2SO_4	30.0		H 949
			SO_4 5949

Soil water working solution

Pipette 10.0 ml soil water stock solution into a 100 ml volumetric flask. Make up with distilled water and homogenize.

Concentrations of the soil water working solution.

----------------------------------$mmol_c.m^{-3}$----------------------------------

Na	275	F	25
K	177	Cl	225
Ca	500	NO_3	1175
Mg	300	SO_4	900
Al	1000	HCO_3	100
NH_4	75	H_2PO_4	2
H+	100		
Σ+	2427	Σ-	2427

Collected water samples are sometimes alkaline. Special care should be taken when collecting and analysing these samples. A synthetic water sample for this kind of samples is very difficult to conserve. Precise measurement of pH and hydrogen carbonate in this synthetic sample is hardly possible.

Preparation of a synthetic alkaline water solution

First pipette HCl, HNO_3 and H_2SO_4 into a 1 litre beaker. Dissolve $CaCO_3$ in this acid mixture. Boil gently for a few minutes to remove CO_2. Fill the beaker to approximately 800 ml with ultra pure water. Add while stirring $NaHCO_3$, $MgSO_4$, KCl and KNO_3. Bubble CO_2 gas (2 bubbles.sec^{-1}) while stirring until all the chemicals are dissolved. Finally add silica and stir for another 48 hours. Bubble with CO_2 (1 bubble.sec^{-1}). Transfer to a 1 litre volumetric flask. Make up to volume with ultra pure water and homogenize. Pour into a 1 litre bottle. Add 0.5 ml chloroform to preserve the solution. Bubble another few minutes with CO_2 gas (1 bubble.sec^{-1}) above the liquid level and close the flask. Keep in the refrigerator.
Before analysis bubble the stock solution with CO_2 for a few minutes. This solution is used as synthetic standard.

Composition of the synthetic alkaline water solution.

Reagent	Weight mg	mls.	$mmol_c.m^{-3}$
CaCO3	250.2		Ca 5000
			HCO_3 3458
$NaHCO_3$	71.4		850
$MgSO_4$	30.0		500
KCl	7.1		100
KNO_3	5.1		50
HCl		5.00	Cl 494
HNO_3		2.25	NO_3 453
H_2SO_4		3.00	SO_4 595
H_2CO_3		gas	
$SiO_2.nH_2O$	17.5		H_4SiO_4 250

The stock solution is also the working solution.

Concentration of the working solution.

-----------------------------------mmol$_c$.m^{-3}-----------------------------------

Na	850	Cl	594
K	150	NO_3	503
Ca	5000	SO_4	1095
Mg	500	HCO_3	4308
Σ+	6500	Σ-	6500

H_4SiO_4	250

Remarks

- In acid solutions,carbonate is removed as CO_2.

- Molarities of the acids have to be checked.

- Use a micro balance to weigh small amounts of chemicals.

- Silica is weighed in hydrated form and corrected for water content by determining loss on ignition.

References

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B04: pH

Principle

The pH is measured with a pH meter, using a glass combination electrode, saturated with potassium chloride.

Apparatus

Orion Research pH meter, model 701A
Orion combination pH electrode, type 91-56.
Magnetic stirrer.

Reagents

Buffer pH 7.00 ampoule (Merck 9887, phosphate titrisol).
Buffer pH 4.00 ampoule (Merck 9884, citrate hydrochloric acid titrisol).
Filling solution of 4 M KCl saturated with AgCl (Orion 90-00-11).
Potassium chloride (KCl) p.a.

> Potassium chloride saturated (4 M).

Weigh 26 gram of KCl into a 400 ml beaker. Add distilled water. Dissolve as much as possible. Transfer into a 100 ml volumetric flask and make up to volume with distilled water. Homogenize.

> pH 7.00 buffer.

Transfer quantitatively an ampoule (pH 7.00) into a 500 ml volumetric flask with distilled water. Make up to volume with distilled water and homogenize.

> pH 4.00 buffer.

Transfer quantitatively an ampoule (pH 4.00) into a 500 ml volumetric flask with distilled water. Make up to volume with distilled water and homogenize.

Procedure

Fill a small polypropylene tube with buffer pH 7.00. Immerse the electrode in the buffer. Stir very slowly and adjust the pH-meter to pH 7.00. Fill another tube with buffer pH 4.00. Immerse the electrode in this buffer and adjust to pH 4.00. Adjust the meter to the sample temperature. Fill a tube with sample. Immerse the electrode into the sample. Stir very slowly and read the pH in 2 decimals after two minutes.

Table of standard conductivity and temperature of solution.

temp.	0.005 M KCl	0.010 M KCl
25° C	716 μS.cm^{-1}	1413 μS.cm^{-1}
24	704	1386
23	691	1359
22	678	1332
21	665	1305
20	652	1278
19	639	1252
18	626	1225
17	613	1199
16	600	1173.

Remarks

- Temperature is very important when measuring conductivity. Regularly check the temperature, or better use a thermostated waterbath.

- Test solution and samples should have the same temperature.

- Each conductivity cell has its own cell constant.

- Use the 0.010 M KCl test solution at conductivities above 1000 μS.cm^{-1}.

References

- Electrochemical data by Dobos, 1975. Elsevier Scientific Publishing Company. Elsevier, The Netherlands.

- Philips, 1985. Users manual digital conductivity meter.

B06: INORGANIC CARBON

Principle

A water sample (up to 250 µL) is automaticallly injected into a reaction vessel where carrier gas is flowing in the form of tiny bubbles in a 25 % H_3PO_4 solution. Only inorganic carbon (including carbonates) is decomposed to become CO_2 which is detected by the non-dispersive infrared gas analyzer (NDIR). Carrier gas is pure oxygen. Concentration is calculated through comparison to standards.

Apparatus

Hamilton injection syringe (250 µl).
T.O.C. analyzer (Shimadzu, type 5000) with autosampler (type ASI 5000).
Ultra pure water apparatus with carbon filter (milli-Q).

Reagents

Oxygen (pure carrier gas).
Phosphorus acid 85% (H_3PO_4) p.a.
Sodium carbonate (Na_2CO_3) p.a.
Sodium hydrogen carbonate ($NaHCO_3$) p.a.

100 mg. L^{-1} stock $NaHCO_3/Na_2CO_3$ solution.

Use ultra pure water. Weigh 630 mg of $NaHCO_3$ and 88.3 mg of Na_2CO_3 into a 1 litre volumetric flask. Dissolve, and make up to volume with ultra pure water and homogenize. Keep in the dark. Prepare weekly.

Phosphoric acid (25%).

Slowly add 74 ml H_3PO_4 85% to 150 ml ultra pure water in a 250 ml volumetric flask. Cool and make up to volume. Homogenize.

Standards

Pipette respectively: 0.00, 5.00, 10.0, 20.0, 30.0, 40.0, and 50.0 ml stock solution into 100 ml volumetric flasks. Make up to volume with ultra pure water and homogenize. Concentrations are respectively:

Blank:	0.00 mg.L^{-1} inorganic carbon
Standard 1:	5.00 mg.L^{-1} inorganic carbon
Standard 2:	10.0 mg.L^{-1} inorganic carbon
Standard 3:	20.0 mg.L^{-1} inorganic carbon
Standard 4:	30.0 mg.L^{-1} inorganic carbon
Standard 5:	40.0 mg.L^{-1} inorganic carbon
Standard 6:	50.0 mg.L^{-1} inorganic carbon

Prepare daily.

Procedure

Set the instrument according to the manufacturer's instructions. Fill autosampler and run standards and samples in triplicate.

Remarks

- It is very important to use an UHQ water apparatus with a carbon filter or boiled distilled water just before preparing stock and standard solutions in order to remove dissolved CO_2. If ultra pure water is not present, use freshly boiled distilled or demineralized water.

- The carbon concentration of the blank can be attributed to CO_2 gas. Calculations of low concentrations of inorganic carbon can be done through correction with blank values.

- Stock solution should not be kept too long (about 1 week).

- When the inorganic carbon concentrations are very low, only prepare standards of 0.00, 5.00 and 10.00 mg.L^{-1}. The blank correction is very important in this case, and more blanks might be included.

References

- Shimadzu, 1992. T.O.C. analyzer instruction manual for model 5000.

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- Small, J.W., 1980. New advances in T.O.C. analysis. Pollution Engineering Magazine, September:66-69.

- Small, R.A., T.W. Lowry and E.M. Ejzak, 1986. Oxidation and detection techniques in T.O.C. analysis. International Laboratory. February issue.

B07: TOTAL CARBON

Principle

A total carbon combustion tube is filled with oxidation catalyst and heated to 680°C. Carrier gas (pure oxygen at 150 ml.min^{-1} flowrate) is supplied into this tube. A sample is injected into the catalyst. The carrier gas, which contains combustion products from the TC combustion, flows through the inorganic carbon reaction vessel. It is sent through a halogen scrubber and water remover into a sample cell in a NDIR detector where CO_2 is measured. The NDIR outputs a signal which generates a peak whose area is calculated by a data processor. The concentration in samples is calculated through comparison to standards.

Apparatus

Hamilton injection syringe (250 µL).
T.O.C. analyzer (Shimadzu, type 5000) with autosampler (type ASI 5000)
Ultra pure water apparatus with carbon filter (UHQ-water).

Reagents

Oxygen (pure carrier gas).
Phosphorus acid 85% (H_3PO_4) p.a.
Platinum catalyst (Shimadzu, art. no. 638-92069-01)
Potassium hydrogen phthalat, dried at 105° C ($KHC_8H_4O_4$) p.a.

Phosphoric acid 25%.

Slowly add 74 ml H_3PO_4 (85%) to 150 ml ultra pure water in a 250 ml volumetric flask. Cool and make up to volume. Homogenize. Fill the inorganic carbon reaction vessel with this solution.

500 mg.L^{-1} total carbon stock solution.

Weigh 1.0628 gram of $KHC_8H_4O_4$ into a 1 litre volumetric flask. Dissolve in 800 ml ultra pure water. Make up with ultra pure water and homogenize. Keep in the dark. Prepare weekly.

Standards

Pipette respectively: 0.00, 5.00, 10.0, 15.0, and 20.0 ml carbon stock solution into 100 ml volumetric flasks. Make up with ultra pure water and homogenize. The concentrations are respectively:

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Blank :	0.0 mg.L^{-1} total carbon
Standard 1:	25.0 mg.L^{-1} total carbon
Standard 2:	50.0 mg.L^{-1} total carbon
Standard 3:	75.0 mg.L^{-1} total carbon
Standard 4:	100.0 mg.L^{-1} total carbon

Prepare daily.

Procedure

Set the instrument according to the manufacturer's instructions. Inject automatically (maximum injection volume = 100 µl). Run standards and samples in triplicate.

Remarks

- In order to remove CO_2, it is very important to use freshly prepared ultra pure water.

- The carbon concentration of the blank is attributed to CO^2 in the UHQ-water.

References

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B08: SUM of ORGANIC ACIDS (S.O.A)

Many waters are brownish or yellowish in colour. This indicates the presence of organic acids. These acids significantly contribute to water acidity or negative charge. When the pH equals the pK of the acid, approximately 50 % of the acid is dissociated. Carboxylic acids are the main functional groups at pK of about 7 or lower. Oliver (1983) found mean carboxyl contents of 5.1 - 13.4 μeg.mg^{-1} organic carbon in samples containing fulvic and humic acids. Hendriksen *et al.* (1979) found 5.5 μeg.mg^{-1} organic carbon. Depending on the samples, commonly a factor of 6.0 (in seawater: 10.0) is used.

Oliver (1983) found that the mass action quotient changes dramatically with pH. Organic acids from varied water sources exhibit almost the same dissociation behaviour as a function of pH. Therefore, when the pH of a water sample is known, the mass action quotient can be estimated from the following empirical equation (Oliver 1983):

$$pK = 0.96 + 0.90 \, pH - 0.039 \, pH^2 \tag{1}$$

The problem of estimating the contribution to acidity of humic substances in a natural waters is thus reduced to measuring the humic substances and the pH of the sample.

The difference between total carbon and inorganic carbon is organic carbon (DOC). The sample DOC in mg.l^{-1} is multiplied by 6.0 μmol_c.mg^{-1} DOC to calculate the sum of organic anions. The mass action quotient is estimated from the pH in the formula above.

$$\text{The sum of organic anions} = [A^-] = \frac{10^{-pK} * C_{org.} * 6.0 * 12}{(10^{-pK} + 10^{-pH}) * 1000} \quad mmol_c.m^{-3} \tag{2}$$

mol. mass of carbon = 12

Example

pH = 3.34 and organic carbon = 1900 $mmol_c$.m^{-3}.
Adding the pH value in formula 1 gives:

$$pK = 0.96 + 0.90 * 3.34 - 0.039 * (3.34)^2 = 3.531$$

Substituting this pK value and the organic carbon concentration in the formula 2 (sum organic anions) gives 54 $mmol_c$.m^{-3} [A$^-$].

References

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B09: DISSOLVED ORGANIC CARBON FRACTIONATION

Principle

Dissolved organic carbon (D.O.C.) is fractionated according to the procedure of De Leenheer and Huffman (1976). Firstly there is a separation in a hydrophobic and hydrophilic organic solute fraction and secondly there is a separation into acid, base and neutral hydrophobic and hydrophilic organic solute fractions. Organic carbon of the sample fractions is determined by analyzing total and inorganic carbon on a T.O.C. analyzer. The method can be used for watersamples with up to 25 mg.L^{-1} dissolved organic carbon and a conductivity of less than 2,000 μS.cm^{-1} at 25°C.

Definitions

Distribution coefficient (k').

The distribution coefficient (k') is the mass of solute sorbed on XAD-8 resin divided by the mass of solute dissolved in water.

Hydrophobic and hydrophilic dissolved organic carbon.

The separation of hydrophobic and hydrophilic organic solute mainly depends on the distribution coefficient (k') for organic solute sorption on Amberlite XAD-8, a nonionic acrylic ester macroreticular resin. The k' values at which half the solute of that k' is either sorbed or desorbed from the XAD-8 resin are used to define the separations between the fractions (ref. 3). For the DOC fractionation, hydrophobic solutes are defined as those solutes that are over 50% retained on XAD-8 at a given ratio of resin to water passed through the column. Hydrophilic solutes are defined as those solutes that are over 50% eluted at the same ratio of resin to water eluent (ref 3). This arbitrary hydrophobic-hydrophilic separation is used for dissolved organic carbon fractionation.

Total hydrophobic DOC fraction.

Total hydrophobic DOC fraction is the DOC fraction of a watersample (adjusted to pH 7) minus the DOC fraction of the eluate from the XAD-8 resin of the acidified (adjusted to pH 2) sample.

Hydrophobic acid DOC fraction.

The hydrophobic acid DOC fraction is the fraction liberated from the XAD-8 resin with alkali after an acidified (pH 2) watersample has passed the column.

Hydrophobic base DOC fraction.

The hydrophobic base DOC fraction is the fraction liberated from the XAD-8 resin with acid after a watersample (adjusted to pH 7) has passed the column.

Hydrophobic neutral DOC fraction.

The hydrophobic neutral DOC fraction is the total hydrophobic DOC fraction minus the hydrophobic acid DOC and hydrophobic base DOC fraction.

Total hydrophilic DOC fraction.

The total hydrophilic DOC fraction is the DOC fraction eluated from the XAD-8 resin after pumping an acidified (pH 2) sample through this XAD-8 resin.

Hydrophilic acid DOC fraction.

The hydrophilic acid DOC fraction is the DOC fraction of an acidified (pH 2) sample percolating through the XAD-8 and cation exchange resin minus the DOC fraction percolating through the XAD-8, cation and anion exchange resin.

Hydrophilic base DOC fraction.

The hydrophilic base DOC fraction is the DOC fraction of an acidified (pH 2) sample percolating through the XAD-8 resin minus the DOC fraction percolating through XAD-8 and cation exchange resin.

Hydrophilic neutral DOC fraction.

The hydrophilic neutral DOC fraction is the DOC fraction of a sample percolating through the XAD 8, cation and anion exchange column.

Samples

All samples should be filtered, as suspended solids will contaminate the resin adsorbants.

Equipment

Anion exchange column (figure 13).
Balance (0.1 mg).
Cation exchange column (figure 13).
Clamps.
Glass erlenmeyer flasks of 300 ml.
Glass wool.
Graduate stoppered cylinders of 25 ml.
Graduate stoppered cylinders of 200 ml.
pH electrode (Orion type 91-56 SC).
pH meter (Orion type 701 A).
Silicon tubing (2*4 mm).
Soxhlet extraction apparatus.
Teflon tubing (4*2 mm).
TOC analyzer (Shimadzu 5000, including ESU-1 and ASI-5000 autosampler)
Tubing column adaptors (figure 13).
Tubing pump (Gilson minipuls 2).
XAD-8 column (figure 13)

Reagents

Acetonitrile (CH_3CN) p.a.
Anion exchange resin (Bio Rad AG-MP-1, 20-50 mesh).
Buffer pH=4.00 ampoule.
Buffer pH=7.00 ampoule.
Buffer pH=12.0 ampoule.
Cation exchange resin (Bio Rad AG-MP-50, 20-50 mesh).
Diethyl ether (($C_2H_5)_2O$) p.a.
Hydrochloric acid 37% (HCl) p.a.
Methanol (CH_3OH) p.a.
Potassium hydrogen phthalat ($KHC_8H_4O_4$) p.a.
Sodium carbonate (Na_2CO_3) p.a.
Sodium hydroxide ampoules (0.1 M and 1.0 M)
Sodium hydrogen carbonate ($NaHCO_3$) p.a.
Ultra pure (carbon free) water.
XAD-8 resin (20-50 mesh).

Sodium hydroxide (0.1 M)

Transfer quantitatively a NaOH (0.1 M) ampoule into a 1 litre volumetric flask. Make up to volume with ultra pure water and homogenize. Prepare daily.

Sodium hydroxide (1 M)

Transfer quantitatively a NaOH (1 M) ampoule into a 1 litre volumetric flask. Make up to volume with ultra pure water and homogenize. Prepare daily.

Sodium hydroxide (2 M).

Transfer quantitatively two NaOH (1.0 M) ampoules into a 1 litre volumetric flask. Make up to volume with ultra pure water and homogenize. Prepare daily.

Hydrochloric acid (0.1 M)

Pour 8 ml HCl (37%) in a 1 litre volumetric flask, containing 500 ml ultra pure water. Make up to volume with ultra pure water and homogenize.

Hydrochloric acid (1 M)

Pour 80 ml HCl (37%) in a 1 litre volumetric flask, containing 500 ml ultra pure water. Make up to volume with ultra pure water and homogenize.

Hydrochloric acid (2 M)

Pour 160 ml HCl (37%) in a 1 litre volumetric flask, containing 500 ml ultra pure water. Make up to volume with ultra pure water and homogenize.

1000 mg.L^{-1} total carbon stock solution.

Weigh 2.1256 gram of KHC$_8$H$_4$O$_4$ (dried at 105°C) and transfer to a 1 litre beaker. Dissolve in 800 ml ultra pure water and transfer to a 1 litre volumetric flask. Make up to volume with ultra pure water and homogenize.

100 mg.L^{-1} inorganic carbon stock solution.

Weigh 630.0 mg of NaHCO$_3$ and 88.3 mg of Na$_2$CO$_3$. Transfer to a 1 litre beaker. Dissolve in 800 ml ultra pure water and transfer to a 1 litre volumetric flask. Make up to volume with ultra pure water and homogenize.

Standards

Pipette respectively: 0.00, 1.00, 2.00, 3.00, 4.00, and 5.00 ml total carbon stock solution into 50 ml volumetric flasks. Make up to volume with ultra pure water and homogenize. The concentrations are respectively:

blank:	0 mg.L^{-1} total carbon
standard 1:	20 mg.L^{-1} total carbon
standard 2:	40 mg.L^{-1} total carbon
standard 3:	60 mg.L^{-1} total carbon
standard 4:	80 mg.L^{-1} total carbon
standard 5:	100 mg.L^{-1} total carbon

High concentrations of total carbon can be measured with a high total carbon standard serie by pipetting the following volumes: 0.0, 5.00, 10.0, 15.0, 20.0, and 25.0 ml total carbon stock solution into 50 ml volumetric flasks. Make up to volume with ultra pure water and homogenize. The concentrations are respectively:

blank:	0 mg.L^{-1} total carbon
standard 1:	100 mg.L^{-1} total carbon
standard 2:	200 mg.L^{-1} total carbon
standard 3:	300 mg.L^{-1} total carbon
standard 4:	400 mg.L^{-1} total carbon
standard 5:	500 mg.L^{-1} total carbon

Pipette respectively: 0.00, 5.00, 10.0, 15.0, and 20.0 ml inorganic carbon stock solution into 100 ml volumetric flasks. Make up to volume with ultra pure water and homogenize. Concentrations are respectively:

blank:	0.0 mg.L^{-1} inorganic carbon
standard 1:	5.0 mg.L^{-1} inorganic carbon
standard 2:	10.0 mg.L^{-1} inorganic carbon
standard 3:	15.0 mg.L^{-1} inorganic carbon
standard 4:	20.0 mg.L^{-1} inorganic carbon

Cleaning and purifying procedures

Glassware.

Before use rinse all the glassware with ultra pure water and place in a furnace at 250°C to remove carbon.

Glass wool.

Purify fine glass wool by Soxhlet extraction with methanol for 24 hours.

XAD-8 resin.

Purify the XAD-8 resin by slurrying with NaOH (0.1 M) in a glass stoppered erlenmeyer flask. Decant after a few minutes and again add NaOH (0.1 M). Leave it for 24 hours. Decant and slurry in methanol. Leave for 1 hour. Decant the methanol. Repeat this step another five times. Transfer the resin into a 250 ml Soxhlet tube. Extract 24 hours in methanol. Replace the methanol and extract another 24 hours in respectively methanol, acetonitrile and diethyl ether. Store the resin in methanol in a glass-stoppered erlenmeyer flask.

Cation exchange resin.

Transfer the resin (AG-MP-50) into the Soxhlet tube with methanol. Extract the resin with methanol for 24 hours. Replace the mathanol and repeat again. Store the resin in methanol in a glass-stoppered erlenmeyer flask.

Anion exchange resin.

Transfer the resin (AG-MP-1) into a 250 ml Soxhlet tube with methanol. Extract the resin with methanol for 24 hours. Replace the methanol and extract for another 24 hours. Store the resin in methanol in a glass-stoppered erlenmeyer flask.

Column packing and final purification

Column packing.

Place a purified glass wool plug at the bottom or on the indentations of the columns (figure 13). Fill the different columns by pouring the purified resins slurried in methanol into the columns. Fill the columns slowly under an angle (45°) to let the air escape. Place a glass wool plug above the XAD-8 resin bed. Always keep liquid above the resin in the column.

Final purification.

The XAD-8 column is connected to teflon tubing and purified by pumping consecutively 500 ml ultra pure water, 50 ml HCl (0.1 M), 50 ml CH_3OH and 100 ml ultra pure water through the column at a rate of 4 ml.min^{-1}. Connect the cation exchange column to the teflon tubing and pump respectively 100 ml ultra pure water, 100 ml NaOH (1.0 M), 100 ml HCl (1.0 M) and 50 ml ultra pure water through the column at a rate of 4 ml.min^{-1}. Connect the anion exchange column to

Figure 13. DOC columns

XAD-8 column

1 cm   8 cm   1 cm

Cation exchange column

10 cm   1 cm

Anion exchange column

18 cm

18/7 Ball and socket ground glass joints: 6 mm OD * 2 mm ID

Columns: 11 mm OD * 7 mm ID

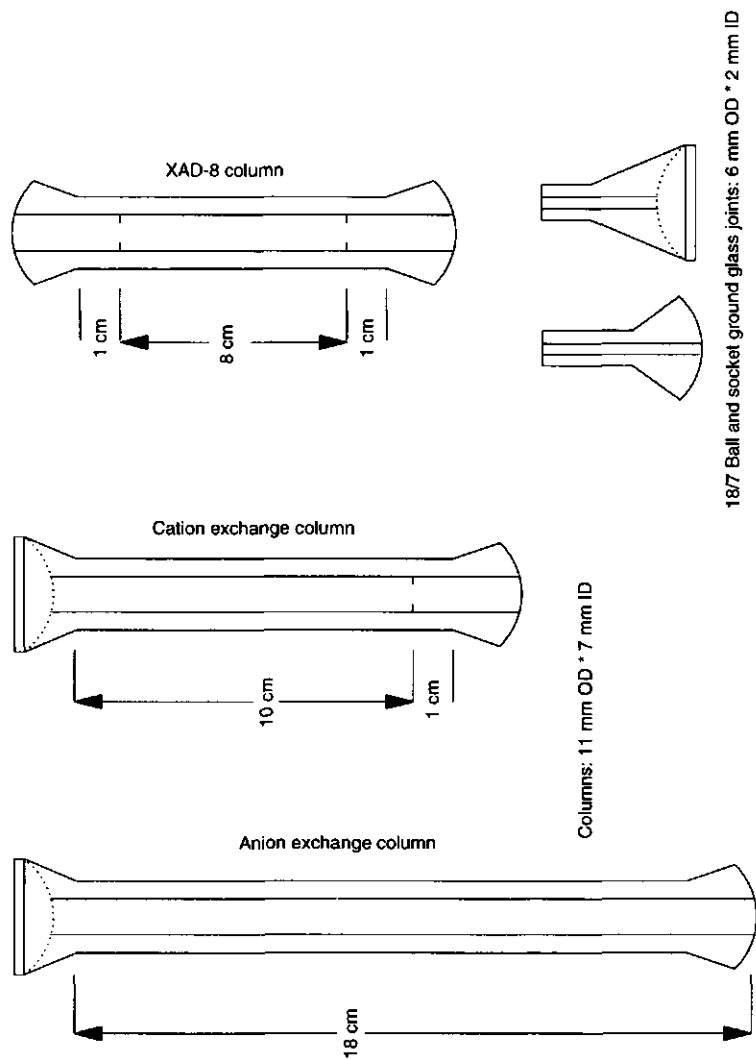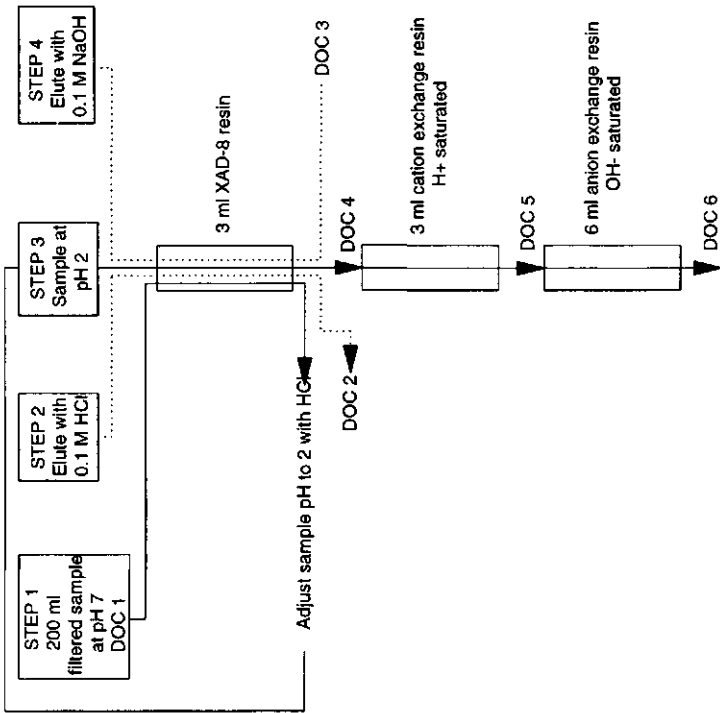# Figure 14. Fractionation scheme

the transfer tubing and pump respectively 100 ml ultra pure water, 100 ml HCl (1.0 M), 100 ml NaOH (2 M) and 50 ml ultra pure water at a speed of 4 ml.min^{-1}. Purify this anion exchange column just before analysis of a sample. Clamp the columns together in the following order: first the XAD-8 column, thereafter the cation exchange column and, finally, the anion exchange column (fig 14). Rinse the connected columns with ultra pure water for at least 5 hours at a rate of 1 ml.min^{-1}. Disconnect the XAD-8 column and pump respectively 50 ml NaOH (0.1 M) and 100 ml ultra pure water through the XAD-8 column.

Analysis

Adjust a watersample dropwise with NaOH (1 M) to pH 7. Pump this sample (DOC 1) through the XAD-8 column at 2 ml.min^{-1}. Collect 160 ml of the eluate in a 200 ml graduated glass cylinder. Stopper. Rinse the column with exactly 20 ml ultra pure water and collect this too in the same 200 ml glass cylinder. Stopper. In this way totally 180 ml sample is collected. Pump HCl (0.1 M) through the XAD-8 column at 1 ml.min^{-1} until 23 ml are collected (DOC 2) in a 25 ml graduated glass cylinder. Stopper. Adjust (dropwise) the pH of the collected 180 ml sample to pH 2 with HCl (37%). Again clamp the columns in the same order. Pump the 180 ml of the acidified watersample through the columns. Discard the first 50 mls. Collect the next 23 ml of eluate in a 25 ml graduated glass cylinder (DOC 6). Stopper. Disconnnect the anion exchange column and collect another 23 ml of eluate in a 25 ml glass graduated cylinder (DOC 5). Stopper. Disconnect the cation exchange column and collect another 23 ml of eluate in a 25 ml glass graduated cylinder (DOC 4). Stopper. Pump the remainder of the sample through the XAD-8 column. Pump NaOH (0.1 M) through the XAD-8 column and collect the first 23 ml of eluate in a 25 ml glass graduated cylinder (DOC 3). Stopper. Shake the stoppered cylinders before analysis. Determine organic carbon in the different DOC fractions by measuring the total carbon and if necessary (when pH of the sample > 4.5) inorganic carbon.

Calculation

To calculate the organic carbon, subtract the inorganic carbon from the total carbon.

Total hydrophobic DOC (mg.L^{-1}) = DOC 1 - (1.125 * DOC 4).

Total hydrophilic DOC (mg.L^{-1}) = 1.125 * DOC 4.

Hydrophobic base DOC (mg.L^{-1}) = (0.023 * DOC 2) / 0.160.

Hydrophobic acid DOC (mg.L^{-1}) = (0.023 * DOC 3) / 0.160.

Hydrophobic neutral DOC (mg.L^{-1}) = Total hydrophobic DOC - hydrophobic base
DOC - hydrophobic acid DOC.

Hydrophilic base DOC (mg.L^{-1}) = 1.125 * (DOC 4 - DOC 5).

Hydrophilic acid DOC (mg.L^{-1}) = 1.125 * (DOC 5 - DOC 6).

Hydrophilic neutral DOC (mg.L^{-1}) = 1.125 * DOC 6.

1.125 = dilution factor 180 ml/160 ml sample.
0.023 = fraction volume in litres.
0.160 = sample volume in litres.

Remarks

- Samples with a high (>2000 µS.cm^{-1}) electrical conductivity contain inorganic salts which exceed the capacity of the resins.

- NaOH adsorbs CO_2. Therefore ampoules are preferred instead of pellets.

- In practice, it is more difficult to pack the anion column than the XAD-8 and cation exchange resin.

- Don't let the columns get dry.

- Before analysis, the column battery is rinsed with ultra pure water during the night (at a flow rate of 1 ml.min^{-1}).

- Some DOC fractions are concentrated on the columns. Therefore total carbon in these fractions can be high. A high standard series is required then.

- The organic carbon fractionation analysis is a very time-consuming procedure, especially the cleaning procedures are laborious.

- Normally, a high standard series (up to 500 mg.L^{-1} total carbon) does not need a blank as part of the standard series. Samples in this high range can be calculated with the appropriate standards alone. The contribution of the blank is negligible in such samples.

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B10: CARBONATE and HYDROGEN CARBONATE

Principle

Carbonate is present in water samples in considerable amounts when pH > 8.2. One way to determine carbonate is an automatic titration with acid (in this case H_2SO_4) to pH 8.2, or a manual titration using phenolphtaleïn as indicator. Hydrogen carbonate (present in samples with pH up to 8.2) is also (automatically) titrated with acid to pH 4.7 - 4.6 or manually using methylorange as indicator. Here we describe both methods.

Samples

Alkaline water samples contain CO_3^{2-} and HCO_3^-. Because they change very rapidly measure these components immediately after pH measurement.

Apparatus

25 ml ($\pm$ 0.02 ml) burette.
Automatic titrator with pH electrode.
Buffer solutions (pH 4.00, 7.00, 8.00, and 10.0)

Reagents

Ethanol 96% (C_2H_5OH) p.a.
Fresh prepared distilled water (or freshly prepared demineralized water).
Methylorange p.a.
Phenolphtalein p.a.
Sodium carbonate (Na_2CO_3) p.a.
Sulphuric acid ampoule (H_2SO_4) (0.1 M).

Phenolphtaleïn (1 %).

Dissolve 1.0 gram of phenolphtalein in 100 ml ethanol (96%).

Methylorange (0.01 %).

Dissolve 10 mg of methylorange in 100 ml freshly prepared distilled water.

Buffer solutions (pH 4.00, 7.00, 8.00, and 10.0).

Transfer quantitatively the contents of the buffer solutions (ampoules) to 500 ml volumetric flasks. Make up to volume with freshly prepared distilled water and homogenize. Keep in the dark. Prepare pH 8.00 and pH 10.0 buffer solutions daily.

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Sulphuric acid (0.05 M).

Transfer quantitatively the contents of an H_2SO_4 (0.1 M) ampoule to a 2 litre volumetric flask. Make up with freshly prepared distilled water and homogenize. Fill a 25 ml dark burette or in the automatic titrator flask (dark coloured). Use a soda-lime tube to prevent CO_2 entering the solution.

Procedure

Manual.

Pipette 50.0 ml sample into a conical flask of 250 ml. Add 10 drops of phenolphtalein. Titrate with H_2SO_4 (0.05 M) solution from red to colourless (CO_3^{2-}). Add 8 drops of methylorange solution. Titrate further from yellow to red (HCO_3^-).
Titrate also a blank of 50 ml freshly prepared distilled water.

Automatic.

It depends on the pH which pH buffer solutions are necessary to set the pH meter. Normally pH 10.0 and pH 7.00 are taken to set the automatic titrator (pH electrode). Pipette 50.0 ml sample into a 150 ml beaker and titrate to pH 8.2 (CO_3^{2-}). Recalibrate the titrator (electrode) with pH buffer 7.00 and 4.00. Titrate further to pH 4.6 - 4.7. Now CO_3^{2-} is titrated to HCO_3^-. Run a blank also (50 ml freshly prepared distilled water). Check calibration (every hour) buffer pH 10.0.

Remarks

- The molarity of the H_2SO_4 can be checked by titration of an accurately weighed quantity of Na_2CO_3 (waterfree), using phenolphtaleïn.

- Organic acid and silicic acid are titrated as well. This may cause serious errors.

- Titration should be executed as soon as possible after arrival of samples in the laboratory.

- Stir very slowly during titration to minimize CO_2 influence.

- Normally pH buffer pH 10.0 and pH 7.00 are used, sometimes pH 8.00 is used. Prepare buffer solutions above pH 7.00 daily. Keep in the dark.

- To prevent serious errors, regularly check the electrode with buffer solutions. Especially pH 10.00 changes rapidly. Serious errors are prevented this way.

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Example

To titrate 50.0 ml of a sample to pH 8.2, 0.30 ml H_2SO_4 (0.05 M) is used. To titrate further to pH 4.7 - 4.6, 4.70 ml H_2SO_4 (0.05 M) is used.
To titrate 50.0 ml of blank (milli-Q water) to pH 4.7 - 4.6, 0.05 ml H_2SO_4 (0.05 M) is needed. Normally there is no CO_3^{2-} in the blank. Therefore blank should only be subtracted from the titration to HCO_3^-.

Carbonate concentration = 0.30 * 0.05 * 1000/50 * 1000 = 300 $mmol_c.m^{-3}$ CO_3^{2-}.

Hydrogen carbonate = (4.70 - (2 * 0.30) - 0.05) * 0.05 * 1000/50 * 1000 =

4,050 $mmol_c.m^{-3}$ HCO_3^-.

B11: HYDROGEN CARBONATE calculated

Preface

Hydrogen carbonate can be determined in different ways. Firstly, it can be titrated automatically with acid to pH 4.7 - 4.6 or manually with methylorange as indicator. Secondly, if only small volumes of sample are present titration is not possible. Therefore inorganic carbon is determined by injection of a small volume (50 µL) of sample into a T.O.C. (total and inorganic carbon) analyzer. Hydrogencarbonate can be calculated from this inorganic carbon concentration and the pH of the sample.

Method

HCO_3^- can be calculated by multiplying total inorganic carbon with a factor α. This factor has a relation to pH and ionic strength (I) at a certain temperature.

Ionic strength is estimated from the electrical conductivity.

$I = 16*10^{-6}*Ec.$ (Ec in $\mu S.cm^{-1}$).

The factor α can be calculated with the following formula:

$$\alpha = \left(1 + \frac{[H^+]}{\dfrac{f_{H+} * f_{H2CO3} * K_1^{\circ}}{f_H^{++} f_{HCO3}}} + \frac{f(HCO_3^-)}{\dfrac{f_{H+} * f_{CO3}^{2-}}{[H^+]}} * K_2^{\circ}\right)^{-1}$$

K_1° $(H_2CO_3 <\!\!-\!\!> H^+ + HCO_3^-) = 10^{-6.381}$ (20°C)

K_2° $(HCO_3^- <\!\!-\!\!> H^+ + CO_3^{2-}) = 10^{-10.377}$ (20°C).

K_1 = equation constant of the $H_2CO_3 <\!\!-\!\!> H^+ + HCO_3^-$ equilibrium.
K_2 = equation constant of the $HCO_3^- <\!\!-\!\!> H^+ + CO_3^{2-}$ equilibrium.

References

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Table: α values in relation to pH and Ionic strength.

pH	I=0.001	I=0.01	pH	I=0.001	I=0.01
4.5	0.013	0.012	6.5	0.559	0.542
4.6	0.016	0.015	6.6	0.615	0.599
4.7	0.020	0.018	6.7	0.670	0.652
4.8	0.025	0.023	6.8	0.717	0.703
4.9	0.031	0.029	6.9	0.761	0.748
5.0	0.039	0.036	7.0	0.800	0.789
5.1	0.048	0.045	7.1	0.834	0.825
5.2	0.060	0.056	7.2	0.863	0.855
5.3	0.074	0.070	7.3	0.888	0.881
5.4	0.091	0.086	7.4	0.909	0.903
5.5	0.112	0.106	7.5	0.926	0.921
5.6	0.138	0.130	7.6	0.939	0.935
5.7	0.167	0.158	7.7	0.950	0.947
5.8	0.202	0.191	7.8	0.959	0.956
5.9	0.242	0.229	7.9	0.966	0.963
6.0	0.286	0.273	8.0	0.971	0.969
6.1	0.335	0.321	8.1	0.975	0.972
6.2	0.389	0.373	8.2	0.977	0.975
6.3	0.444	0.428	8.3	0.979	0.976
6.4	0.502	0.485	8.4	0.979	0.976

B12: AMMONIUM

Principle

Ammonium is measured colorimetrically as an emerald green complex of ammonium with sodium salicylate, sodium nitroprusside and sodium hypochlorite. The pH is buffered to 12.8-13.0.

Equipment

Computer (with interface).
Folded filters.
Recorder.
Technicon autoanalyzer (II) with autosampler.

Reagents

Ammonium sulphate $(NH_4)_2SO_4$ p.a.
Brij-35 solution.
Hydrochloric acid 37% (HCl) p.a.
Sodium hydroxide 32% solution, special quality for NH_4^+ determination (NaOH).
Sodium hypochlorite (keep in a refrigerator) (NaOCl) p.a.
Sodium nitroprusside $(Na_2Fe(CN)_5NO.2H_2O)$ p.a.
Sodium phosphate, dibasic $(Na_2HPO_4.2H_2O)$ p.a.
Sodium potassium tartrate $(NaKC_4H_4O_6.4H_2O)$ p.a.
Sodium salicylate $(NaC_7H_5O_3)$ p.a.

      Sodium hydroxide stock solution (20%).

Carefully add 625 ml NaOH (32%) solution to 350 ml distilled water in a 1 litre volumetric flask. Cool and make up to volume with distilled water. Homogenize.

      Sodium potassium tartrate stock solution (20%).

Dissolve 200 gram of $NaKC_4H_4O_6.4H_2O$ in 800 ml distilled water in a 1 litre beaker. Transfer to a 1 litre volumetric flask. Make up to volume with distilled water and homogenize.

      Buffer stock solution.

Dissolve 89 gram of $Na_2HPO_4.2H_2O$ in 800 ml hot distilled water in a 1 litre beaker. Cool. Add 50 ml NaOH 32% solution. Cool. Transfer to a 1 litre volumetric flask. Make up to volume with distilled water and homogenize.

Buffer working solution.

Combine 200 ml buffer stock solution and 250 ml $NaKC_4H_4O_6.4H_2O$ stock solution in a 1 litre beaker. Swirl. Add 60 ml NaOH 20% solution. Swirl and cool. Transfer to a 1 litre volumetric flask. Make up to volume with distilled water. Add 1 ml Brij-35 solution and homogenize.

Sodium salicylate/sodium nitroprusside solution.

Dissolve 150 gram of $NaC_7H_5O_3$ and 300 mg of $Na_2Fe(CN)_5NO.2H_2O$ in 800 ml distilled water in a 1 litre beaker. Transfer to a 1 litre volumetric flask. Make up to volume with distilled water. Homogenize. Filter through a folded filter and add 1 ml Brij-35 solution. Homogenize again. Store in a dark bottle.

Sodium hypochlorite (5%).

Add 5.0 ml NaOCl to 80 ml distilled water in a 100 ml volumetric flask. Make up to volume with distilled water and add a few drops of Brij-35 solution. Homogenize. Prepare daily.

Hydrochloric acid (1 M).

Add 80 ml concentrated HCl (37%) to 800 ml distilled water in a 1 litre beaker. Cool. Transfer to a 1 litre volumetric flask. Make up to volume with distilled water and homogenize.

5,000 $mmol.m^{-3}$ ammonium stock solution.

Weigh 330.0 mg of $(NH_4)_2SO_4$ (dried at 105°C) and dissolve in 800 ml distilled water. Transfer into a 1 litre volumetric flask. Make up to volume with distilled water and homogenize.

Standards

Pour 200 ml distilled water and 3 drops of HCl (1 M) into a 250 ml volumetric flask. Pipette 25.0 ml NH_4^+ stock solution. Make up to volume with distilled water and homogenize (Standard 6). Pour a few mls of distilled water and 1 drop HCl (1 M) into 50 ml volumetric flasks. Pipette respectively: 0.00, 5.00, 10.0, 20.0, 30.0, and 40.0 ml of standard 6. Make up to 50 ml with distilled water and homogenize. The concentrations are respectively:

Blank:	0 $mmol.m^{-3}$ NH_4^+
Standard 1:	50 $mmol.m^{-3}$ NH_4^+
Standard 2:	100 $mmol.m^{-3}$ NH_4^+
Standard 3:	200 $mmol.m^{-3}$ NH_4^+
Standard 4:	300 $mmol.m^{-3}$ NH_4^+
Standard 5:	400 $mmol.m^{-3}$ NH_4^+
Standard 6:	500 $mmol.m^{-3}$ NH_4^+

Procedure

Prepare the autoanalyzer for measurement (figure 15) following manufacturer's instructions. Wavelength is 660 nm, flowcell is 1.5 cm. Fill the autosampler with standards and samples. Run at a speed of 30 samples per hour. Calculate the concentration of the samples with standards. Regularly run control samples to check the quality of the analysis. Run blanks to check baseline drift.
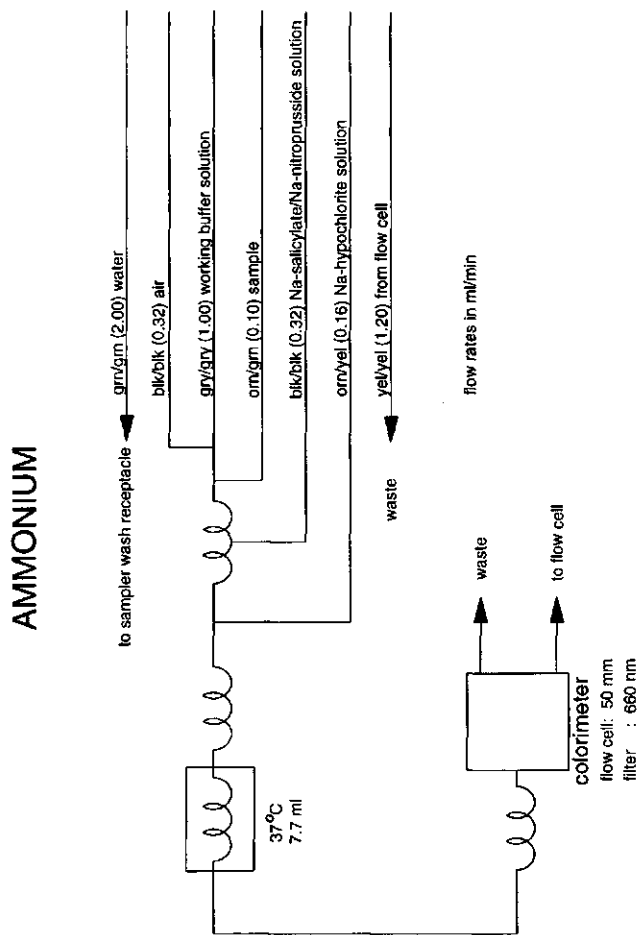
Remarks

- To prevent CO_2 pollution prepare the NaOH solution (20%) directly into a 1 litre volumetric flask.

- Sodium nitroprusside is toxic.

- This method can also be used for soil extracts with KCl. The standard series used is from 0 to 5.0 mg.L^{-1} NH$_4^+$. A flow cell of 50 mm is recommended then.

References

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- Weatherburn, M.W., 1961. Phenol-hypochlorite reaction for determination of ammonia. Analytical Chemistry 39(8):971-974.

Figure 15. Flow scheme for ammonium determination

AMMONIUM

to sampler wash receptacle

grn/grn (2.00) water

blk/blk (0.32) air

grn/grn (1.00) working buffer solution

orn/grn (0.10) sample

blk/blk (0.32) Na-salicylate/Na-nitroprusside solution

orn/yel (0.16) Na-hypochlorite solution

yel/yel (1.20) from flow cell

waste

flow rates in ml/min

37°C
7.7 ml

colorimeter
flow cell: 50 mm
filter : 660 nm

waste

to flow cell

B13: PHOSPHATE

Principle

Phosphate is mixed with molybdate, antimony and ascorbic acid to form a reduced blue coloured phospho molybdenum complex, which is measured colorimetrically at 880 nm with a 5.0 cm flowcell. The pH of the solution is 4.0 .

Equipment

Balance (0.001 mg).
Computer (equipped with an interface).
Glass cylinder 250 ml stoppered.
Recorder.
Technicon autoanalyzer (II) with autosampler.

Reagents

Aerosol-22 solution.
Ammonium molybdate $(NH_4)_6Mo_7O_{24}.4H_2O$ p.a.
Antimony potassium tartrate $(K(SbO)C_4H_4O_6.0.5H_2O$ p.a.
Ascorbic acid $(C_6H_8O_6)$ p.a.
Distilled water.
Hydrochloric acid 37% (HCl) p.a.
Potassium dihydrogen phosphate, dried at 105°C (KH_2PO_4) p.a.
Sodium hydroxide pellets (NaOH) p.a.
Sulphuric acid concentrated 95-97% (H_2SO_4) p.a.

Stable working reagent.

Dissolve 3.0 gram of $(NH_4)_6Mo_7O_{24}.4H_2O$ and 32.9 mg of $K(SbO)C_4H_4O_6.0.5H_2O$ in 400 ml distilled water in a 800 ml beaker. Carefully add 35 ml H_2SO_4 (95-97%). Cool, transfer to a 500 ml volumetric flask and make up to volume with distilled water. Add 1 ml Aerosol-22 solution and homogenize. Prepare daily.

Ascorbic acid.

Dissolve 1.0 gram of $C_6H_8O_6$ in 150 ml distilled water in a 250 ml glass stoppered cylinder. Fill up to 200 ml with distilled water. Stopper. Homogenize. Prepare daily. Keep in the dark.

Hydrochloric acid (1 M).

Add 80 ml HCl (37%) to 800 ml distilled water in a 1 litre beaker. Cool and transfer into a 1 litre volumetric flask. Make up to volume with distilled water and homogenize.

Sodium hydroxide (0.1 M).

Dissolve 4 gram of NaOH pellets in 800 ml distilled water in a 1 litre beaker. Cool. Transfer into a 1 litre volumetric flask. Make up to volume with distilled water. Homogenize.

1.000 mmol(+).m^{-3} H$_2$PO$_4^-$ stock solution.

Weigh 136.1 mg of KH$_2$PO$_4$ (dried at 105°C) and dissolve in 800 ml distilled water in a 1 litre beaker. Transfer into a 1 litre volumetric flask. Make up to volume with distilled water and homogenize.

Standards

Pour 200 ml distilled water and 3 drops HCl (1 M) to a 250 ml volumetric flask. Pipette 5.00 ml H$_2$PO$_4^-$ stock solution. Make up to volume with distilled water. Homogenize (Standard 6). Transfer a few mls distilled water and 1 drop HCl (1 M) to 50 ml volumetric flasks. Pipette from standard 6 respectively: 0.00, 5.00, 10.0, 20.0, 30.0, and 40.0 ml. Make up to 50 ml with distilled water and homogenize. The concentrations are respectively:

Blank: 0.00 mmol$_c$.m^{-3} H$_2$PO$_4^-$
Standard 1:   2.00 mmol$_c$.m^{-3} H$_2$PO$_4^-$
Standard 2:   4.00 mmol$_c$.m^{-3} H$_2$PO$_4^-$
Standard 3:   8.00 mmol$_c$.m^{-3} H$_2$PO$_4^-$
Standard 4:   12.0 mmol$_c$.m^{-3} H$_2$PO$_4^-$
Standard 5:   16.0 mmol$_c$.m^{-3} H$_2$PO$_4^-$
Standard 6:   20.0 mmol$_c$.m^{-3} H$_2$PO$_4^-$

Procedure

Prepare the autoanalyzer for measurement (figure 16) following manufacturer's instructions. Fill the autosampler with standards and samples. Run at a speed of 30 samples per hour. Calculate concentrations of the samples from standards. Regularly run control samples and blanks to check the quality of the analysis and baseline drift.

Remarks

-   If dilution is necessary the antimony concentration should be 0.4 mg Sb per 50 ml final solution.

-   One 1 drop of HCl (1 M) per 50 ml sample or standards is needed to avoid absorbance of phosphate to glassware and bottles.

- After finishing the measurements, rinse the apparatus for 15 minutes with NaOH (0.1 M).

- The number of samples per hour can be varied. We prefer to run 30 samples per hour. With this speed the autoanalyzer system is rinsed sufficiently between two samples.

- Phosphate has to be determined with distilled water. Demineralized water contains silicon, which interferes.

- Use specially cleaned glassware to prepare standards and solutions. Acidify all the glassware with HCl (1 M) and if necessary NaOH (1 M). Keep this glassware separated.

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pure water. Transfer to a 1 litre volumetric flask. Make up to volume with ultra pure water and homogenize.

1.000 g.L^{-1} sulphate stock solution.

Weigh 1.8142 gram of K_2SO_4 (dried at 105° C). Transfer to a 800 ml beaker. Add approximately 600 ml ultra pure water. Dissolve. Transfer to a 1 litre volumetric flask. Make up to volume with ultra pure water and homogenize.

Standards

Pipette respectively 15.0 ml Cl$^-$ stock solution, 30.0 ml NO_3^- stock solution and 30 ml SO_4^{2-} stock solution into a 500 ml volumetric flask (standard 7). Make up with ultra pure water and homogenize. Pipette from standard 7, respectively: 0.00, 5.00, 10.0, 20.0, 30.0, and 40.0 ml in 50.0 ml volumetric flasks. Use ultra pure water as blank. Make up to volume with ultra pure water and homogenize.

Standard:	Cl^{-1}	NO_3^-	SO_4^{2-}
	--------------------------mmol$_c$.m^{-3}-------------------------		
Blank:	0.0	0.0	0
Standard 1:	84.5	96.8	125
Standard 2:	169.0	193.5	250
Standard 4:	338.0	387.1	500
Standard 5:	507.0	580.6	750
Standard 6:	676.1	774.2	1000
Standard 7:	845.1	967.7	1250

Procedure

Set the HPLC according to manufacturer's instructions. Stabilize overnight at a pumpspeed of 0.4 ml.min^{-1}. Adjust the temperature of the refractometer to 35°C and the temperature control module to 38°C. Run standards and samples automatically. Use filtered (0.2μm) samples. Regularly run control samples in a sample series.

Remarks

-   The quality of the water is very important. Use ultra pure quality or double distilled water.

-   Temperature of the column should be a few degrees higher than that of the refractometer.

- Outlet tubing of the refractometer should be above the detection cell.

- Avoid particles in the sample (capillar tubing).

References

- Chrompack Ionosphere-A column analytical procedure.

- Gilson diluter instruction manual.

- Waters H.P.L.C. operating manual.

B15: CHLORIDE by AUTOANALYZER

Principle

The automated procedure for the determination of chloride is based on the liberation of thiocyanate from mercuric thiocyanate by the formation of unionized but soluble mercuric chloride. In the presence of an iron (III) ion, the liberated thiocyanate forms a coloured iron (III) thiocyanate complex. Colour intensity is proportional to the original chloride concentration.

Apparatus

Computer (with interface).
Recorder.
Technicon autoanalyzer (II) with autosampler.

Reagents

Brij-35 solution.
Iron (III) nitrate $(Fe(NO_3)_3.9H_2O)$ p.a.
Mercuric thiocyanate $(Hg(SCN)_2)$ p.a.
Methanol (CH_3OH) p.a.
Nitric acid 65% (HNO_3) p.a.

Mercuric thiocyanate stock solution.

Pour 500 ml methanol into a 1 litre beaker. Add 4.17 gram of $Hg(SCN)_2$. Dissolve and transfer to a 1 litre volumetric flask and make up to volume with methanol. Homogenize. Filter through a paper filter. Keep in a dark bottle.

Iron (III) nitrate stock solution (20.2 %).

Weigh 202 gram of $Fe(NO_3)_3.9H_2O$ in a 1 litre beaker. Dissolve in distilled water. Carefully add 32 ml 65% HNO_3 and mix. Cool. Transfer to a 1 litre volumetric flask and make up to volume with distilled water. Homogenize. Filter through a paper filter and store in an amber coloured reagent bottle.

Chloride colour reagent.

Pour 150 ml stock $Hg(SCN)_2$ solution into a 1 litre beaker. Add 150 ml stock $Fe(NO_3)_3.9H_2O$ solution. Mix. Transfer to a 1 litre volumetric flask and make up to volume with distilled water. Add 1 ml Brij-35. Homogenize.

1.000 $g.L^{-1}$ chloride stock solution.

Dissolve 1.648 gram of NaCl (dried at 105°C) in about 600 ml distilled water in a 1 litre beaker. Transfer to a 1 litre volumetric flask. Make up to volume with distilled water and homogenize.

Standards

Pipette 2.00 ml Cl⁻ stock solution into a 100 ml volumetric flask. Make up to volume with distilled water and homogenize. Pipette from this solution respectively: 0.00, 5.00, 10.0, 15.0, 20.0, and 25.0 ml into 50 ml volumetric flasks. Make up to volume with distilled water and homogenize. The concentrations are:

Blank:	0.00 mg.L^{-1} Cl⁻
Standard 1:	2.00 mg.L^{-1} Cl⁻
Standard 2:	4.00 mg.L^{-1} Cl⁻
Standard 3:	6.00 mg.L^{-1} Cl⁻
Standard 4:	8.00 mg.L^{-1} Cl⁻
Standard 5:	10.0 mg.L^{-1} Cl⁻

Procedure

Prepare the autoanalyzer (figure 5) for measurement following manufacturer's instructions (figure 17). Wavelength is 480 nm, flowcell is 15 mm. Fill autosampler with standards and samples. Run at a speed of 30 samples per hour. Run control samples and blanks to check the quality of the measurement and baseline drift.
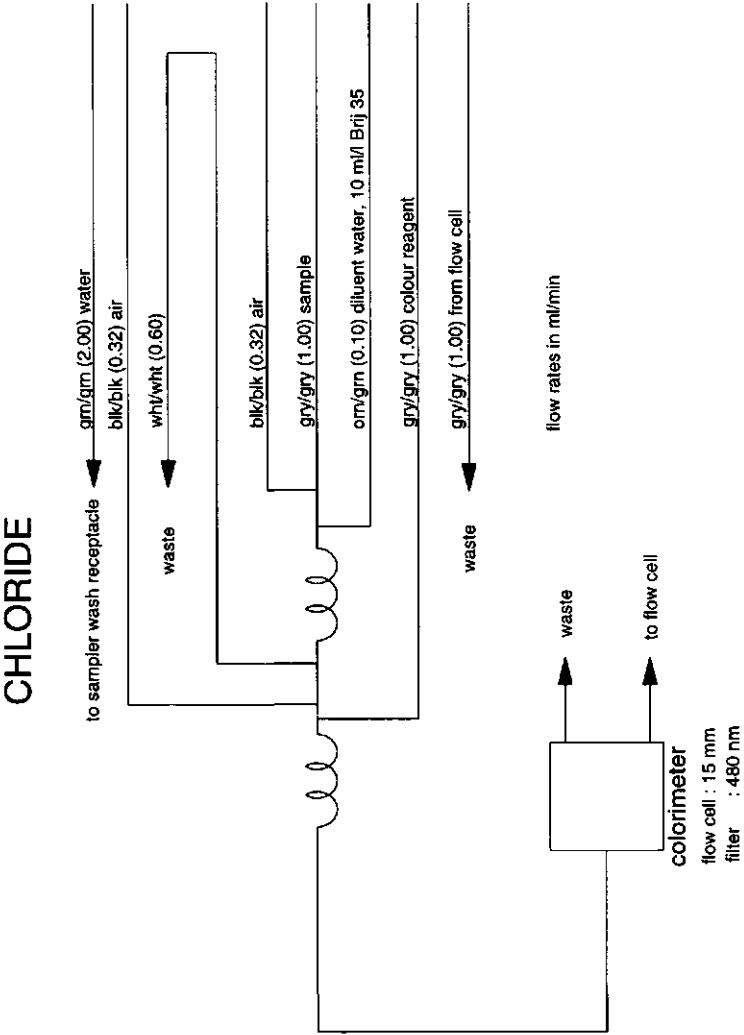
Remarks

- Collect the effluent from the chloride channel in a separate waste container. Place it in a well ventilated area.

- Take good care of mercury disposal (safety aspects).

- It is allowed to use demineralized water.

- After measurement, rinse thoroughly with water and if necessary with diluted HCl (2 M) and/or diluted NaOH (1 M).

References

- O'Brien, B.E., 1962. Automatic analysis of chlorides in sewage. Waste Engineering.

- Technicon autoanalyzer (II) Manual.

- Zall, D.M., et al., 1956. Analytical Chemistry, Vol 28.

Figure 17. Flow scheme for chloride determination

CHLORIDE

to sampler wash receptacle — grn/grn (2.00) water

blk/blk (0.32) air

waste — wht/wht (0.60)

blk/blk (0.32) air

gry/gry (1.00) sample

orn/grn (0.10) diluent water, 10 ml/l Brij 35

gry/gry (1.00) colour reagent

waste — gry/gry (1.00) from flow cell

flow rates in ml/min

waste

to flow cell

colorimeter
flow cell : 15 mm
filter : 480 nm

B16: NITRATE and NITRITE

Principle

Nitrate is reduced to nitrite in a copper-cadmium reductor column at pH 7.5. In acidic conditions, the nitrite forms a reddish purple azo dye with N-1-naphtyl-ethylene-di-hydrochloride and sulphanil-amide. This colour is measured with an autoanalyzer at 520 nm and with a 1.5 cm flowcell.

Apparatus

Cadmium reductor column, U-shaped glass tube (about 15 cm long and an ID of 2 mm) provided with autoanalyzer connections.
Computer (+ interface).
Four-way valve.
Funnels (small).
Recorder.
Technicon autoanalyzer (II) including 6" membrane-dialyzer.

Reagents

Ammonia (NH_4OH) p.a.
Ammonium chloride (NH_4Cl) p.a.
Brij-35 (wetting agent).
Cadmium granules (particle size 0.3 - 0.8 mm) p.a.
Copper-II-sulphate ($CuSO_4.5H_2O$) p.a.
Hydrochloric acid 37% (HCl) p.a.
N-1-naphtyl-ethylene-di-hydrochloride ($C_{10}H_2HNCH_2CH_2NH_2.2HCl$) p.a.
Sodium nitrate ($NaNO_3$) p.a. dried at 105°C.
Sulphanil-amide ($4-NH_2C_6H_4SO_2NH_2$) p.a.
Sulphuric acid 96-98% (H_2SO_4) p.a.

Hydrochloric acid (2 M).

Add 80 ml HCl (37%) to 350 ml distilled water in a 800 ml beaker. Cool and mix. Transfer to a 500 ml volumetric flask. Make up to volume. Homogenize.

Copper-II-sulphate 20 g.L^{-1}.

Dissolve 20 gram of $CuSO_4$ in 800 ml acidified distilled water (1 drop H_2SO_4 96-98%) in a 1 L beaker. Transfer to a 1 litre volumetric flask. Make up to volume with distilled water and homogenize.

Ammonium chloride buffer (25 g.L^{-1}).

Dissolve 50 gram of NH$_4$Cl in approximately 1500 ml distilled water in a 2 litre beaker. Add 6 ml of NH$_4$OH. The pH should be approximately 6.5. Transfer to a 2 litre volumetric flask. Make up to volume with distilled water. Add 1.0 ml Brij-35 solution. Homogenize.

Working SAN solution.

Pour approximately 600 ml distilled water in a 1 litre beaker. Carefully add 50 ml HCl 37%. Cool and mix. Add 5.0 gram of 4-NH$_2$C$_6$H$_4$SO$_2$NH$_2$. Dissolve. Transfer to a 1 litre volumetric flask and make up to volume. Add 0.5 ml Brij-35 solution. Homogenize. Keep this solution in a dark container.

Working NED solution.

Dissolve 0.5 gram of C$_{10}$H$_2$HNCH$_2$CH$_2$NH$_2$.2HCl in about 800 ml distilled water in
a 1 litre beaker. Transfer to a 1 litre volumetric flask. Add 0.5 ml Brij-35 solution. Make up to volume and homogenize. Keep this solution in a dark container.

Cadmium reductor column

Wash procedure cadmium granules.

Wash 3 - 4 gram of cadmium granules 3 times during 1 minute with 10 ml HCl (2 M). Rinse the granules till acid free. Add 50 ml CuSO$_4$ solution and swirl for 3 minutes. Rinse thoroughly with distilled water to remove flocculated copper. Now the granules are ready for use.

Filling the reductor column.

Fill the U-shaped column with NH$_4$Cl buffer solution. Insert the activated cadmium granules in both sides of the column with 2 funnels. Prevent air bubbling in the column. Vibrate now and then. Fill up to approximately 5 cm from the top. Seal both ends with plugs of quartz wool pre-wetted in NH$_4$Cl buffer solution. Connect to the 4-way valve. **Avoid air bubbles.**

1.000 mg.L^{-1} nitrate stock solution.

Dissolve 1.3707 g of NaNO$_3$ in approximately 800 ml in a 1 litre beaker. Transfer quantitatively to a 1 litre volumetric flask. Make up to volume with distilled water and homogenize.

Standards

Pipette respectively: 0.00, 2.00, 4.00, 6.00, 8.00, and 10.0 ml of the nitrate stock solution into 100 ml volumetric flasks containing 50 ml distilled water. The concentrations are:

Blank:	0.0 mg.L^{-1} NO$_3$
Standard 1:	20.0 mg.L^{-1} NO$_3$
Standard 2:	40.0 mg.L^{-1} NO$_3$
Standard 3:	60.0 mg.L^{-1} NO$_3$
Standard 4:	80.0 mg.L^{-1} NO$_3$
Standard 5:	100.0 mg.L^{-1} NO$_3$

Procedure

Prepare the autoanalyzer for measurement (figure 18) following the manufacturer's instructions. Wavelength is 520 nm, flowcell is 1.5 cm. Rinse the instrument with distilled water for half an hour. Adjust the colorimeter. Transfer the tubing from the water into the reagents. After 15 minutes, connect the Cd-reductor column to the system by means of the 4-way valve. Wait another half hour. Re-adjust the colorimeter. Now the instrument is ready for use. After measurement, disconnect the Cd-reductor column prior to changing the tubing from reagent to distilled water. Rinse the system for at least one hour.

Remarks

- Store activated cadmium in a dark place.

- The membrane dialyzer excludes interfering elements like organic substances, colloids and solid particles. Only 10-15 % of the sample passes the membrane.

- Only buffered NH_4Cl solutions should enter the Cd-reductor column. Connect and disconnect the column in time.

- Air bubbles in the Cd-reductor column will shorten its lifetime.

References

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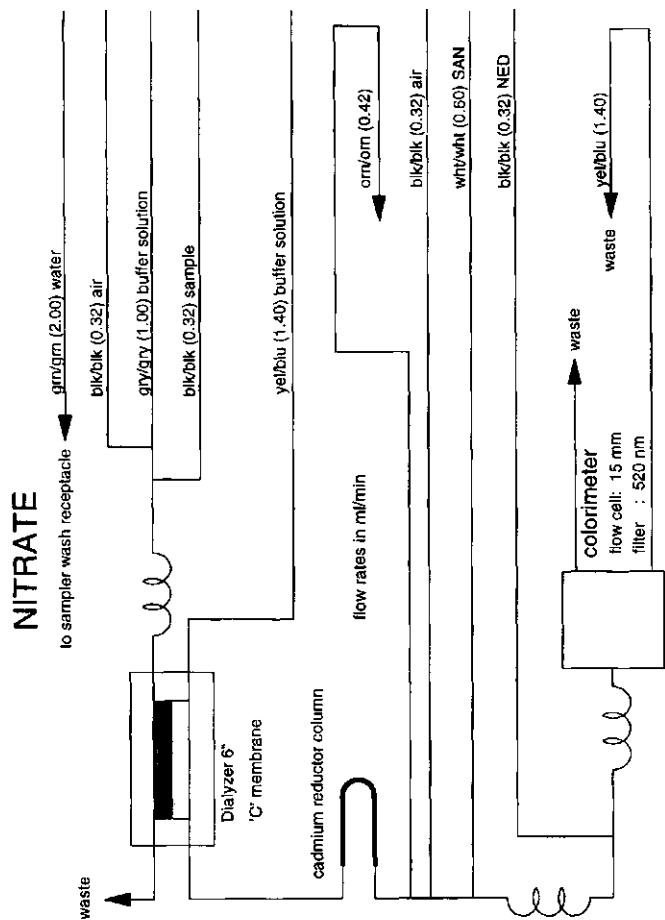
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Acknowledgement

Figure 18. Flow scheme for nitrate determination

NITRATE

to sampler wash receptacle

grn/grn (2.00) water

blk/blk (0.32) air

gry/gry (1.00) buffer solution

blk/blk (0.32) sample

yel/blu (1.40) buffer solution

orn/orn (0.42)

blk/blk (0.32) air

wht/wht (0.60) SAN

blk/blk (0.32) NED

yel/blu (1.40)

waste

flow rates in ml/min

Dialyzer 6"
'C' membrane

cadmium reductor column

colorimeter
flow cell: 15 mm
filter : 520 nm

waste

waste

B17: SULPHIDE

Principle

Preservation of water samples for sulphide determination can be done by adding zinc acetate. Under acidic conditions, metal sulphides can form a coloured complex with p-amino dimethyl analine and iron (III) methylene blue. This reaction is specific for sulphide. The methylene blue colour is measured at 670 nm after 10 minutes.

Sample

Pool water or soil extract water is used to determine sulphide. After sampling it must be immediately injected into a 30 ml serum bottle with septum, which contains a $Zn(CH_3COO)_2.2H_2O$ solution (figure 1: *chapter collection and preservation*). The serum bottle is also flushed with nitrogen gas.

Apparatus

Hamilton syringe (0-100 µl).
Injection needles.
Serum bottles (glass, 30 ml) with screwcap and septum.
Spectrophotometer 55E, 1 cm cuvet (Perkin Elmer).
Waterbath.

Reagents

Acetic acid glacial 100% (CH_3COOH) p.a.
Boiled distilled water.
Hydrochloric acid (37%) (HCl) p.a.
Iodium solution ampoule 0.05 M (I_2) p.a.
Iron (III) ammonium sulphate ($Fe(NH_4)(SO_4)_2.12H_2O$) p.a.
Nitrogen gas, high quality, S-510-H (N_2).
P-amino dimethyl aniline ($C_8N_2H_{12}$) p.a.
Potassium dichromate ($K_2Cr_2O_7$) p.a.
Potassium iodide (KI) p.a.
Sodium hydrogen carbonate ($NaHCO_3$) p.a.
Sodium sulphide ($Na_2S.xH_2O$) (x=7-9) p.a.
Sodium thiosulphate ($Na_2S_2O_3.5H_2O$) p.a.
Starch solution ($C_6H_{10}O_5)_n$ p.a.
Sulphuric acid 95-97% (H_2SO_4) p.a.
Zinc acetate ($Zn(CH_3COO)_2.2H_2O$) p.a.

Zinc acetate solution (2%).

Weigh 11.96 gram of $Zn(CH_3COO)_2.2H_2O$ into a 800 ml beaker. Add 400 ml distilled water and dissolve. Add 0.1 ml CH_3COOH and transfer to a 500 ml volumetric flask. Make up to volume and homogenize.

P-amino dimethyl aniline.

Pour tap water into a 1 litre beaker. Put the reagent bottle into this tap water and allow the tap water to warm to approximately 40°C on a waterbath. Weigh (approximately) 0.25 gram of $C_8N_2H_{12}$ (40°C) into a 250 ml beaker. Add 100 ml distilled water and carefully 50 ml H_2SO_4 (95-97%). Quickly transfer to a 250 ml volumetric flask. Cool, make up to volume with distilled water, and homogenize. Prepare daily.

Iron (III) ammonium sulphate (1.25%).

Weigh 25 gram of $Fe(NH_4)(SO_4)_2.12H_2O$ into a 250 ml beaker. Add 150 ml of distilled water and 5 ml H_2SO_4 (95-97%). Transfer to a 200 ml volumetric flask. Make up to volume and homogenize.

Potassium dichromate solution.

Weigh exactly 0.9805 gram of $K_2Cr_2O_7$. Transfer to a 800 ml beaker. Dissolve in 400 ml distilled water. Transfer to a 1 litre volumetric flask. Make up with distilled water and homogenize.

Starch solution.

Make a paste of 1.0 gram of $(C_6H_{10}O_5)_n$ with a little water and pour the paste with constant stirring into 100 ml boiling water. Boil for 1 minute. Allow to cool. Keep in a stoppered bottle.

Iodium solution (0.05 M).

Transfer an ampoule, containing I_2 (0.05 M) into a 1 litre volumetric flask. Make up to volume with boiled water and homogenize. Transfer to a dark bottle and keep in the dark.

Hydrochloric acid (6 M)

Pour 200 ml distilled water into a 600 ml beaker. Add 250 ml HCl 37% and cool. Transfer to a 500 ml volumetric flask and make up with distilled water. Homogenize.

Sodium thiosulphate solution (approx. 0.005 M).

Dissolve 1.24 gram of $Na_2S_2O_3.5H_2O$ in 400 ml distilled water in a 800 ml beaker. Transfer to a 1 litre volumetric flask. Make up with distilled water and homogenize.

Standardized sodium thiosulphate.

Add some solid KI and some solid $NaHCO_3$ to a 250 ml erlenmeyer flask, containing 100 ml boiled distilled water. Pour 12 ml HCl (6 M) and dissolve. Pipette 5.00 ml $K_2Cr_2O_7$ solution. Stopper the erlenmeyer flask and leave it for 5 minutes in the dark. Titrate to colourless with $Na_2S_2O_3.5H_2O$ (0.005 M). Add 2 ml $C_6H_{10}O_5)_n$ solution at the end of the titration. Run at least in triplicate. Run three blanks. Calculate the molarity of the $Na_2S_2O_3.5H_2O$.

Sodium sulphide solution (approximately 0.005 M).

Dissolve about 1 gram of $Na_2S.xH_2O$ in 400 ml distilled water in a 800 ml beaker. Transfer into a 1 litre volumetric flask and homogenize. Prepare daily. Keep in the dark. Determine the molarity of this solution with $Na_2S_2O_3.5H_2O$ (see sodium thiosulphate).

Standardizing sodium sulphide.

Pipette 10.0 ml $Na_2S.xH_2O$ solution into a 250 ml erlenmeyer flask, containing 100 ml boiled distilled water. Swirl. Pipette 2.00 ml I_2 solution and immediately add 5.0 ml HCl (6 M). Titrate to colourless with $Na_2S_2O_3.5H_2O$ solution (0.005 M). Add 2 ml $C_6H_{10}O_5)_n$ solution at the end of the titration. Run at least in triplicate. Run three blanks. Calculate the molarity of the $Na_2S.xH_2O$ solution.

Standards

Prepare serum bottles with septum, containing 5.00 ml boiled distilled water and 5.00 ml $Zn(CH_3COO)_2.2H_2O$ solution. Flush with N_2 gas. Pipette with a Hamilton syringe in triplicate respectively: 0.00, 5.00, 10.0, 15.0, 20.0, 25.0, 30.0, 40.0, 50.0, and 60.0 µl into separate serum bottles. Swirl. Pipette (inject) 1.00 ml $C_8N_2H_{12}$, swirl and pipette immediately 0.4 ml $Fe(NH_4)(SO_4)_2.12H_2O$. Swirl again. Wait 10 minutes and read the extinction at 670 nm. Calibrate a standard curve. The concentrations of the standard series are approximately 0, 2, 4, 6, 8, 10, 12, 16, 20, and 24 $µM.L^{-1}$ sulphide.

Procedure

Pipette 5.00 mls $Zn(CH_3COO)_2.2H_2O$ (2%) solution into a 25 ml bottles with septum. Close the bottles and flush 10 seconds with N_2 gas. Collect a water sample at the sample plot and immediately pipette (inject) 5.00 ml sample into a bottle. Shake a few times and take this sample to the laboratory.
In the laboratory, pipette (inject) 1.00 ml $C_8N_2H_{12}$ to this solution, swirl and immediately pipette (inject) 0.4 ml $Fe(NH_4)(SO_4)_2.12H_2O$. Swirl again. Wait 10 minutes and measure the extinction at 670 nm. Run the standard series in triplicate under the same conditions.

Remarks

- The sample should be free of air as much as possible.

- It is impossible to weigh $C_8N_2H_{12}$ at room temperature (20° C). Therefore warm the bottle to approximately 40° C.

- To prevent sulphide in the blank, boil distilled water and keep the bottles closed under N_2 gas.

References

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B18: ALUMINIUM

Principle

Before analysis, the watersample is acidified with HCl (1 M) to approximately pH 4.2. Aluminium (Al^{3+}) is measured with an autoanalyzer system by means of a brown coloured aluminium pyrocatechol violet complex, at a wavelength of 580 nm. Final pH should be between 6.0 - 6.2. Flowcell is 15 mm.

Samples

Samples should be acidified before analysis. Add 1 drop HCl (1 M) to about 20 ml sample and wait at least 24 hours before measurement. Monomeric Al^{3+} is measured now.

Equipment

Balance (0.1 mg).
Computer (+interface).
Finn pipette (0 - 5.000 ml).
pH meter + electrode.
Recorder.
Technicon autoanalyser (II) with autosampler.

Reagents

Aluminium ampoule 1.000 g.
Ammonium acetate (CH_3COONH_4) p.a.
Brij-35 solution.
Glacial acetic acid (CH_3COOH) p.a.
Hydrochloric acid 37% (HCl) p.a.
Hydroxyl ammonium chloride ($NH_2OH.HCl$) p.a.
1.10 Ortho phenanthroline ($C_{12}H_9N_2Cl.H_2O$) p.a.
Polyvinyl alcohol (P.V.A.) p.a.
Pyrocatechol violet ($C_{19}H_{14}O_7S$) p.a.

Hydrochloric acid (1 M).

Carefully add 80 ml HCl (37%) to 800 ml distilled water in a 1 litre beaker. Cool and transfer to a 1 litre volumetric flask. Make up to volume with distilled water and homogenize.

1.10 Ortho phenanthroline stock solution.

Dissolve in a 1 litre beaker 3.9 gram of polyvinyl alcohol (P.V.A.) in approximately 800 ml hot

distilled water. Add 12.5 gram of $NH_2OH.HCl$ and 125 mg of $C_{12}H_9N_2Cl.H_2O$. Cool and transfer with distilled water to a 1 litre volumetric flask. Make up to volume with distilled water. Homogenize. Store in a polyethylene bottle.

1.10 Ortho phenanthroline working solution.

Transfer (cylinder) 100 ml stock $C_{12}H_9N_2Cl.H_2O$ solution to a 1 litre volumetric flask. Make up with distilled water to the mark. Add 0.5 ml Brij-35 solution. Homogenize.

Pyrocatechol violet solution.

Dissolve 37.5 mg of $C_{19}H_{14}O_7S$ in 50 ml distilled water in a 250 ml beaker. Transfer to a 100 ml volumetric flask. Make up to volume with distilled water and homogenize. Prepare daily. Store in a pyrex glass bottle.

Ammonium acetate/acetic acid buffer.

Weigh 500 gram of CH_3COONH_4 in a 5 litre beaker. Add 4.5 litre distilled water. Dissolve. Adjust with CH_3COOH to pH 6.3(pH meter). Transfer into a 5 litre polyethene bottle with stopper. Homogenize. The pH should be between 6.2-6.0.

1.000 g.L^{-1} aluminium stock solution.

Transfer quantitatively an aluminium ampoule, containing 1.000 gram of aluminium into a 1 litre volumetric flask. Make up with distilled water and homogenize.

Standards

Pour approximately 150 ml distilled water into a 250 ml volumetric flask. Add 3 drops HCl (1 M), swirl and pipette 2.25 ml aluminium stock solution. Make up with distilled water and homogenize. Pipette from this solution respectively:
0.00, 2.50, 5.00, 10.0, 15.0, 20.0, and 25.0 ml into 50 ml volumetric flasks, containing 15 ml of distilled water and 1 drop HCl (1 M).

------Al in **ionic** concentrations------

Blank:	0 mmol$_c$.m^{-3} Al^{3+}
Standard 1:	50 mmol$_c$.m^{-3} Al^{3+}
Standard 2:	100 mmol$_c$.m^{-3} Al^{3+}
Satndard 3:	200 mmol$_c$.m^{-3} Al^{3+}
Standard 4:	300 mmol$_c$.m^{-3} Al^{3+}
Standard 5:	400 mmol$_c$.m^{-3} Al^{3+}
Standard 6:	500 mmol$_c$.m^{-3} Al^{3+}

Procedure

Follow manufacturer's instructions to set up the instrument (figure 19). Rinse the autoanalyzer with distilled water (containing 1 ml.L^{-1} of Brij-35) for half an hour.

Adjust the instrument. Run with reagents. Adjust the colorimeter. Start measurement with standards followed by samples. Regularly run two or three blanks and control samples to check the quality of the analysis and baseline drift. Calculate afterwards.
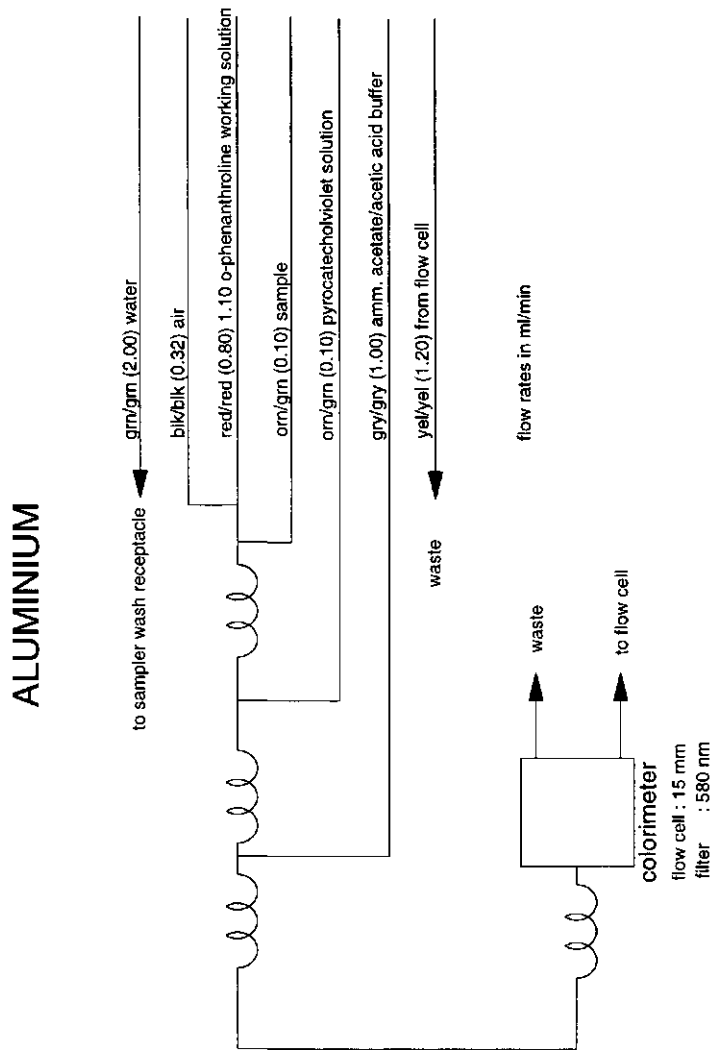
Remarks

- Rinse the autosampler afterwards with HCl (1 M) for 20 minutes and distilled water, containing 1 ml Brij-35.L^{-1} for one hour.

- For concentrations below 125 mmol(+).m^{-1} Al^{3+}, pipette respectively: 0.00, 5.00, 10.0, 15.0, 20.0, and 25.0 ml into 200 ml volumetric flasks, containing 3 drops HCl (1 M). Change the sample tube of the autoanalyzer (0.32 instead of 0.1 mm ID).

- 1.10 Ortho phenanthroline solution is added to mask iron.

- Test the Finn pipette before use.

- After measurement, rinse the instrument with HCl (1 M) and water for one hour.

References

- Technicon modification method no. 188-75 E.

- Technicon instrumental autoanalyzer instruction.

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Figure 19. Flow scheme for aluminium determination

ALUMINIUM

to sampler wash receptacle ← grn/grn (2.00) water

blk/blk (0.32) air

red/red (0.80) 1.10 o-phenanthroline working solution

orn/grn (0.10) sample

orn/grn (0.10) pyrocatecholviolet solution

gry/gry (1.00) amm. acetate/acetic acid buffer

yel/yel (1.20) from flow cell

waste

flow rates in ml/min

waste

to flow cell

colorimeter
flow cell : 15 mm
filter   : 580 nm

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B19: SILICON

Principle

The determination of dissolved silicon is based on the reduction of silico molybdate in acidic solution to molybdenum blue by ascorbic acid. The wavelength is 660 nm. Flowcell is 15 mm.

Equipment

Computer (+ interface).
Cylinder of 250 ml (stoppered).
Pipette (2.00 - 10.0 ml).
Polyethylene or polypropylene beakers and 1 litre volumetric flasks.
Recorder.
Technicon autoanalyzer (II) with autosampler.

Reagents

Acetone (CH_3COCH_3) p.a.
Aerosol-22 solution.
Ammonium molybdate ($(NH_4)_6Mo_7O_{24}.H_2O$) p.a.
Ascorbic acid ($C_6H_8O_6$) p.a.
Distilled water.
Hydrochloric acid 37% (HCl) p.a.
Oxalic acid ($C_2H_2O_4.2H_2O$) p.a.
Silicon ampoule (1 gram of silica in hydrochloric acid)
Sulphuric acid concentrated 95-97% (H_2SO_4) p.a.

Ammonium molybdate solution.

Dissolve 10.0 grams of $NH_4)_6Mo_7O_{24}.H_2O$ in approximately 800 ml distilled water in a 1 litre beaker. Add 2.8 ml H_2SO_4 (95-97%). Cool and transfer to a 1 litre volumetric flask. Make up to volume with distilled water. Homogenize and store in a polyethylene bottle. Prepare daily.

Oxalic acid.

Dissolve 50.0 grams of $C_2H_2O_4).2H_2O$ in 800 ml distilled water in a 1 litre beaker. Transfer into a 1 litre volumetric flask. Make up to volume with distilled water. Homogenize and store in a polyethylene bottle.

Ascorbic acid.

Dissolve 1.0 gram of $C_6H_8O_6$ in 190 ml distilled water in a 250 ml cylinder. Add 10 ml CH_3COCH_3 and stopper. Add 0.5 ml Aerosol-22 solution. Shake well. Prepare daily.

Hydrochloric acid (1 M).

Add 80 ml HCl (37%) to 800 ml distilled water in a 1 litre beaker. Cool and transfer to a 1 litre volumetric flask. Make up to volume with distilled water and homogenize.

1.000 g.L^{-1} silicon stock solution.

Transfer quantitatively a silicon ampoule, containing 1.000 gram of silica in HCl into a 1 litre polypropylene volumetric flask. Make up with distilled water and homogenize. Store in a tightly stoppered polyethylene or polypropylene bottle.

Standards

Pipette 7.00 ml silicon stock solution into a 250 ml polypropylene volumetric flask, containing 100 ml distilled water and 3 drops of HCl (1 M). Make up to volume with distilled water and homogenize. Pipette from this solution, respectively:
0.00, 5.00, 10.0, 15.0, 20.0, and 25.0 ml into 50 ml volumetric flasks containing 10 ml distilled water and 1 drop HCl (1 M). Ionic concentrations are respectively:

Blank:	0 mmol$_c$.m^{-3} Si
Standard 1:	100 mmol$_c$.m^{-3} Si
Standard 2:	200 mmol$_c$.m^{-3} Si
Standard 3:	300 mmol$_c$.m^{-3} Si
Standard 4:	400 mmol$_c$.m^{-3} Si
Standard 5:	500 mmol$_c$.m^{-3} Si

Procedure

Rinse the autoanalyzer for half an hour with distilled water containing 1 ml.L^{-1} Aerosol-22. Follow manufacturer's instructions to optimize the system. Connect the reagent tubes (figure 20) in the following order: $(NH_4)_6Mo_7O_{24}.H_2O$, $C_2H_2O_4.2H_2O$ and finally $C_6H_8O_6$. Run the autoanalyzer for another 30 minutes. Adjust the colorimeter and start measurement. Run standards followed by samples. Check the instrument with blanks and artificial samples of known concentrations to check the baseline drift and quality of the measurement. Disconnect the reagents in reverse order. Rinse for at least 1 hour with distilled water, containing 1 ml.L^{-1} Aerosol-22.

Remarks

-   Oxalic acid is added to the sample stream before the addition of ascorbic acid to eliminate interference from phosphates.

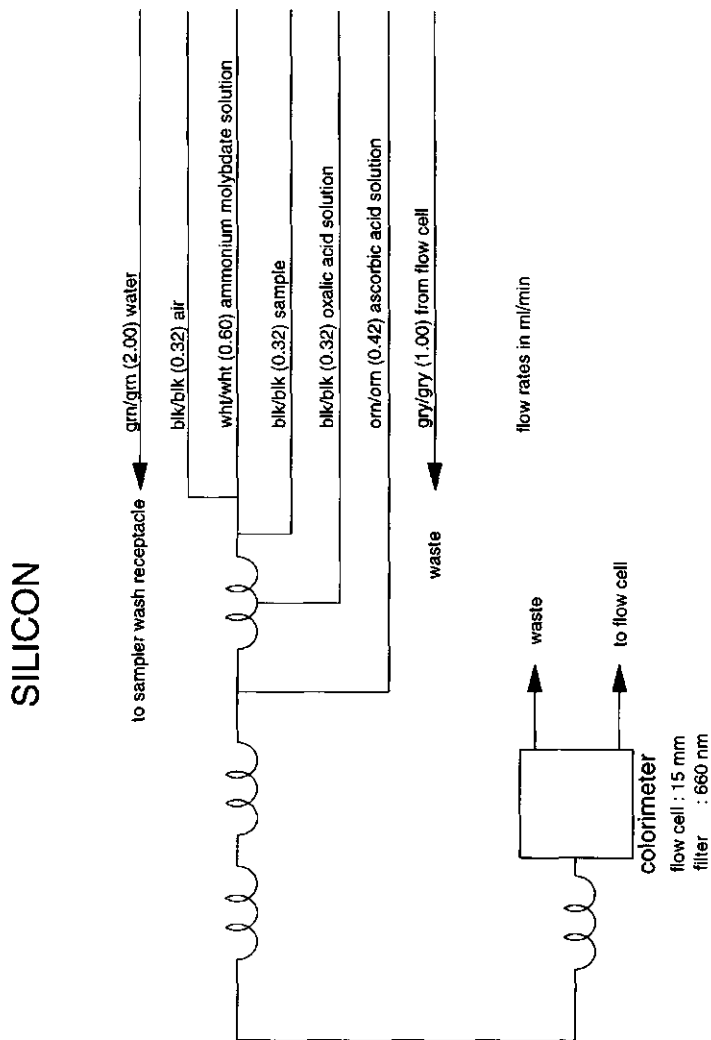-   Tannin, large amounts of iron, and sulfide may interfere.

- To avoid staining, glassware should not be used .

- Reagents should be prepared with distilled water.

- Rinse the system with NaOH (1 M) solution followed by HCl (1 M) solution and finally with distilled water.

References

- Kolthoff, I.M., and E.B. Sandell, 1945. Textbook of quantitative inorganic analysis. Reference Edition. New York.

- Technicon industrial autoanalyzer instruction.

- Technicon industrial method no. 105-71W.

Figure 20. Flow scheme for silicon determination

SILICON

to sampler wash receptacle

grn/grn (2.00) water

blk/blk (0.32) air

wht/wht (0.60) ammonium molybdate solution

blk/blk (0.32) sample

blk/blk (0.32) oxalic acid solution

orn/orn (0.42) ascorbic acid solution

gry/gry (1.00) from flow cell

waste

flow rates in ml/min

waste

to flow cell

colorimeter

flow cell : 15 mm
filter   : 660 nm

B20: SODIUM

Principle

Sodium is measured by flame emission spectrometry on an A.A.S./A.E.S. at 589.0 nm wavelength. A lean blue air acetylene flame is used. To control ionization, an alkali salt (cesium) is added. Linear range at 589.0 nm and 0.2 nm slit is up to 1.0 $mg.L^{-1}$ Na.

Samples

Cesium chloride is added to the acidified water sample (1 drop HCl (1 M) per 20 ml sample) to get a 1,000 $mg.L^{-1}$ Cs matrix.

Apparatus

Balance (0.1 mg).
Gilson autosampler, model 222.
Perkin Elmer A.A.S./A.E.S., type 560.

Reagents

Cesium chloride (CsCl) p.a.
Hydrochloric acid 37% (HCl) p.a.
Sodium ampoule (1.000 gram) p.a.

Hydrochloric acid (1 M).

Carefully add 20 ml HCl (37%) to 150 ml distilled water in a 400 ml beaker. Cool. Transfer to a 250 ml polypropylene volumetric flask. Make up to volume with distilled water and homogenize.

Cesium chloride (5,000 $mg.L^{-1}$ Cs).

Dissolve 6.3341 gram of CsCl (dried at 105° C) in 800 ml distilled water in a 1 litre beaker. Transfer to a 1 litre polypropylene volumetric flask. Make up to volume with distilled water and homogenize.

Cesium chloride (1,666 $mg.L^{-1}$ Cs).

Dissolve 2.1105 gram of CsCl (dried at 105° C) in 800 ml distilled water in a 1 litre beaker. Transfer to a 1 litre polypropylene volumetric flask. Make up to volume with distilled water and homogenize.

Cesium chloride (1,250 mg.L^{-1} Cs).

Dissolve 1.5835 gram of CsCl (dried at 105° C) in 800 ml distilled water in a 1 litre beaker. Transfer to a 1 litre polypropylene volumetric flask. Make up to volume with distilled water and homogenize.

Cesium chloride (1,111 mg.L^{-1} Cs).

Dissolve 1.4074 gram of CsCl (dried at 105° C) in 800 ml distilled water in a 1 litre beaker. Transfer to a 1 litre polypropylene volumetric flask. Make up to volume with distilled water and homogenize.

1.000 g.L^{-1} sodium stock solution.

Transfer quantitatively a sodium ampoule, containing 1.000 gram of sodium in HCl, into a 1 litre polypropylene volumetric flask. Make up to volume with distilled water and homogenize. Store in a polypropylene bottle.

Standards

Pipette 2.00 ml sodium stock solution into a 200 ml polypropylene volumetric flask. Make up to volume with distilled water and homogenize. Pipette from this solution respectively: 0.00, 5.00, 10.0, and 20.0 ml into 50 ml polypropylene volumetric flasks. Add 10 ml 5,000 mg.L^{-1} CsCl solution to blank and standards.

Blank:	0.00 mg.L^{-1} Na
Standard 1:	1.00 mg.L^{-1} Na
Standard 2:	2.00 mg.L^{-1} Na
Standard 3:	4.00 mg.L^{-1} Na

Procedure

Dependent on the sodium concentration in the sample, dilute respectively:
4.00 ml sample with 1.00 ml CsCl solution (5,000 mg.L^{-1} Cs); 2.00 ml sample with 3.00 ml CsCl solution (1,666 mg.L^{-1} Cs); 1.00 ml sample with 4.00 ml CsCl solution (1,250 mg.L^{-1} Cs) or 0.50 ml sample with 4.50 ml CsCl solution (1,111 mg.L^{-1} Cs). Follow manufacturer's instructions to measure the concentrations.

Remarks

- To avoid staining, don't use glassware.

- Stock solutions can be used for several months.

- Cesium background should be 1,000 mg.L^{-1} Cs.

- Normally, standards and samples have to be prepared in the same way. To optimize the instrument (A.E.S.), mls of standard solutions are used. If standards should be prepared as samples (5 ml final solution) there would be no liquid left for measurement. Therefore standard solutions are prepared in volumetric flasks. Errors (compare standards and samples) are minimized by checks.

References

- Gilson Autosampler Instruction Manual.

- Perkin Elmer Manual Instruction.

- Perkin Elmer Analytical Methods.

Appendix.

For ion balance calculations, concentrations have to be expressed in mmol(+).
By diluting respectively: 0.50, 1.00, 2.00, and 4.00 ml sample to 5.00 ml final solution, the concentration in the samples can be read out directly by using the recalculated standard series.

----------------Sodium in $mmol_c.m^{-3}$------------------

------------------dilution---------------------

Sodium standard	0.50->5.00	1.00->5.00	2.00->5.00	4.00->5.00 ml
0.00 $mg.L^{-1}$	0	0	0	0
1.00 $mg.L^{-1}$	435	217	109	54
2.00 $mg.L^{-1}$	870	435	217	109
4.00 $mg.L^{-1}$	1740	870	435	217

B21: POTASSIUM

Principle

Potassium is measured by flame emission spectrometry on an A.E.S. at 766.5 nm wavelength with a lean blue air acetylene flame and 2.0 nm slit. Ionization is controlled by the addition of cesium chloride. A specific red filter is used. Linear range is 0-2.0 mg.L^{-1} K.

Samples

To prevent ionization 1,000 mg.L^{-1} Cs is added to samples and standards.

Apparatus

Autosampler (Gilson, model 222).
Atomic emission spectrometer (Perkin Elmer, A.E.S., type 560).
Balance (0.1 mg).

Reagents

Cesium chloride (CsCl) p.a.
Hydrochloric acid 37% (HCl) p.a.
Potassium ampoule (1.000 gram) p.a.

> Hydrochloric acid (1 M).

Carefully add 80 ml HCl (37%) to 800 ml distilled water in a 1 litre beaker. Cool. Transfer to a 1 litre volumetric flask. Make up to volume with distilled water and homogenize.

> Cesium chloride (5,000 mg.L^{-1} Cs).

Dissolve 6.3341 gram of CsCl (dried at 105° C) in 800 ml distilled water in a 1 litre beaker. Transfer to a 1 litre polypropylene volumetric flask. Make up to volume with distilled water and homogenize.

> Cesium chloride (1,666 mg.L^{-1} Cs).

Dissolve 2.1105 gram of CsCl (dried at 105° C) in 800 ml distilled water in a 1 litre beaker. Transfer to a 1 litre polypropylene volumetric flask. Make up to volume with distilled water and homogenize.

> Cesium chloride (1,250 mg.L^{-1} Cs).

Dissolve 1.5835 gram of CsCl (dried at 105° C) in 800 ml distilled water in a 1 litre beaker. Transfer to a 1 litre polypropylene volumetric flask. Make up to volume with distilled water and homogenize.

Cesium chloride (1,111 mg.L^{-1} Cs).

Dissolve 1.4074 gram of CsCl (dried at 105° C) in 800 ml distilled water in a 1 litre beaker. Transfer to a 1 litre polypropylene volumetric flask. Make up to volume with distilled water and homogenize.

1.000 g.L^{-1} potassium stock solution.

Transfer quantitatively the content of a potassium ampoule, containing 1.000 gram of potassium in HCl, to a 1 litre polypropylene volumetric flask. Make up with distilled water to 1 litre and homogenize. Store in a polypropylene bottle.

Standards

Pipette 2.00 ml potassium stock solution into a 100 ml polypropylene volumetric flask. Make up with distilled water and homogenize. Pipette from this solution respectively: 0.00, 5.00, 10.0, and 20.0 ml into 50 ml polypropylene volumetric flasks. Add 20 ml 5,000 mg.L^{-1} Cs solution to blank and standards.

Blank:	0.00 mg.L^{-1} K
Standard 1:	2.00 mg.L^{-1} K
Standard 2:	4.00 mg.L^{-1} K
Standard 3:	8.00 mg.L^{-1} K

Procedure

Dilution of the samples depends on the potassium concentration. Therefore dilute (automatically) the samples respectively: 4.00 ml sample with 1.00 ml CsCl solution (5,000 mg.L^{-1} Cs); 2.00 ml sample with 3.00 ml CsCl solution (1,666 mg.L^{-1} Cs); 1.00 ml sample with 4.00 ml CsCl solution (1,250 mg.L^{-1} Cs) or 0.50 ml sample with 4.50 ml CsCl solution (1,111 mg.L^{-1} Cs). Follow manufacturer's instructions to measure the concentrations. Calculate contents using the appendix.

Remarks

-   The potassium stock solution can be used a few months. Standard solution must be prepared daily.

-   Matrix must be 1,000 mg.L^{-1} Cs.

References

-   Gilson Autosampler Instruction Manual.

-   Perkin Elmer Instruction Manual.

- Perkin Elmer Analytical Methods.

Appendix

By diluting respectively: 0.50, 1.00, 2.00, and 4.00 ml sample to 5.00 ml final solution, the concentration in the samples can be read directly by using the recalculated standard series.

-------------------Potassium in mmol$_c$.m^{-3}--------------------

-------------------dilution---------------------

Potassium standard	0.5->5.00	1.00->5.00	2.00->5.00	4.00->5.00
0.00 mg.L^{-1}	0	0	0	0
2.00 mg.L^{-1}	512	256	128	64
4.00 mg.L^{-1}	1020	512	256	128
8.00 mg.L^{-1}	2050	1020	512	256

B22: CALCIUM

Principle

Calcium is measured on an A.A.S. at 422.7 nm wavelength and 0.7 nm slit with a lean blue air, acetylene flame. To prevent the formation of stable oxisalts, lanthanum is added. Linear range is up to 5.0 mg.L^{-1} calcium.

Samples

Samples are measured in a 1 % La matrix.

Apparatus

A.A.S. (Perkin Elmer, type 560).
Autosampler (Gilson, model 222).
Balance (0.1 g).
Filters (folded).

Reagents

Calcium ampoule (1.000 gram) p.a.
Hydrochloric acid 37% (HCl) p.a.
Lanthanum oxide (La$_2$O$_3$) p.a.

Lanthanum (5%).

Weigh 58.6 gram of La$_2$O$_3$ in a 1 litre beaker. Add about 800 ml distilled water and 100 ml HCl (37%). Dissolve. Cool and transfer to a 1 litre polypropylene volumetric flask. Make up to volume with distilled water and homogenize. Filter over a folded filter into a 1 litre polypropylene bottle.

Lanthanum (1.66%).

Weigh 19.5 gram of La$_2$O$_3$ in a 1 litre beaker. Add about 800 ml distilled water and 34 ml HCl (37%). Dissolve. Cool and transfer to a 1 litre polypropylene volumetric flask. Make up to volume with distilled water and homogenize. Filter over a folded filter into a 1 litre polypropylene bottle.

Lanthanum (1.25 %).

Weigh 14.7 gram of La$_2$O$_3$ in a 1 litre beaker. Add about 800 ml distilled water and 25 ml HCl (37%). Dissolve. Cool and transfer to a 1 litre polypropylene volumetric flask. Make up to volume with distilled water and homogenize. Filter over a folded filter into a 1 litre polypropylene bottle.

Lanthanum (1.11 %).

Weigh 13.0 gram of La$_2$O$_3$ in a 1 litre beaker. Add about 800 ml distilled water and 23 ml HCl

(37%). Dissolve. Cool and transfer to a 1 litre polypropylene volumetric flask. Make up to volume with distilled water and homogenize. Filter over a folded filter into a 1 litre polypropylene bottle.

1.000 g.L^{-1} calcium stock solution.

Transfer quantitatively a calcium ampoule, containing 1.000 gram of calcium in HCl, to a 1 litre polypropylene volumetric flask. Make up to 1 litre with distilled water and homogenize. Store in a polypropylene bottle.

Standards

Pipette 5.00 ml calcium stock solution into a 100 ml volumetric flask. Make up with distilled water and homogenize. Pipette from this solution respectively:
0.00, 5.00, 10.0, and 20.0 ml into 50 ml polypropylene volumetric flasks. Add 10 ml lanthanum solution (5%) to blank and standards. Make up to volume with distilled water and homogenize.

Blank: 0.00 mg.L^{-1} Ca
Standard 1:   5.00 mg.L^{-1} Ca
Standard 2:   10.0 mg.L^{-1} Ca
Standard 3:   20.0 mg.L^{-1} Ca

Procedure

Samples must also have a lanthanum background. Therefore dilute respectively:
4.00 ml sample with 1.00 ml La$_2$O$_3$ solution (5% La); 2.00 ml sample with 3.00 ml La$_2$O$_3$ solution (1.66% La); 1.00 ml sample with 4.00 ml La$_2$O$_3$ solution (1.25% La) or 0.50 ml sample with 4.50 ml La$_2$O$_3$ solution (1.11% La). For measurement follow manufacturer's instructions to measure the concentrations. For calculation, see appendix.

Remarks

-    Absorption of calcium depends on the fuel/air ratio and the burner height. Maximum sensitivity is obtained with a fuel-rich flame, optimum precision with a fuel lean flame.

-    Final solution should have 1% La matrix.

-    Aluminium, phosphorus, silicon and vanadium give reduction of sensitivity, but addition of lanthanum reduces this interference.

-    It is allowed to use de-ionized water.

Lanthanum (1.25 %).

Weigh 14.7 gram of La_2O_3 in a 1 litre beaker. Add about 800 ml distilled water and carefully 25 ml HCl (37%). Dissolve. Cool and transfer to a 1 litre polypropylene volumetric flask. Make up to volume with distilled water and homogenize. Filter over a folded filter into a 1 litre polypropylene bottle.

Lanthanum (1.11 %).

Weigh 13.0 gram of La_2O_3 in a 1 litre beaker. Add about 800 ml distilled water and carefully 23 ml HCl (37%). Dissolve. Cool and transfer to a 1 litre polypropylene volumetric flask. Make up to volume with distilled water and homogenize. Filter over a folded filter into a 1 litre polypropylene bottle.

1.000 $g.L^{-1}$ magnesium stock solution.

Transfer quantitatively the contents of a magnesium ampoule, containing 1.000 gram of magnesium in HCl, into a 1 litre polypropylene volumetric flask. Make up to volume with distilled water and homogenize. Store in a polypropylene bottle.

Standards

Pipette 5.00 ml magnesium stock solution into a 1 litre volumetric flask. Make up with distilled water and homogenize. Pipette from this solution respectively:
0.00, 5.00, 10.0, and 20.0 ml in 50 polypropylene volumetric flasks. Add 10 ml 5% La_2O_3 solution to blank and standards. Make up to volume with distilled water and homogenize.

Blank: 0.00 $mg.L^{-1}$ Mg
Standard 1:   0.50 $mg.L^{-1}$ Mg
Standard 2;   1.00 $mg.L^{-1}$ Mg
Standard 3:   2.00 $mg.L^{-1}$ Mg

Procedure

Dependent on the magnesium concentration, dilute (automatically): 4.00 ml sample with 1.00 ml La_2O_3 solution (5%); 2.00 ml sample with 3.00 ml La_2O_3 solution (1.66%); 1.00 ml sample with 4.00 ml La_2O_3 solution (1.25%) or 0.50 ml sample with 4.50 ml La_2O_3 solution (1.11 %). Matrix in the final solutions is 1 % La_2O_3. For measurement follow manufacturer's instructions.

Remarks

-       De-ionized water can be used.

-       Ionization may be controlled by the addition of an alkali salt (e.g. KCl).

-        Final solution should contain 1% La.

References

-        Gilson Autosampler Instruction Manual.

-        Perkin Elmer Manual Instruction.

-        Perkin Elmer Analytical Methods.

Appendix

By diluting respectively: 0.50, 1.00, 2.00, and 4.00 ml sample to 5.00 ml final solution, the concentration in the samples can be read out directly by using the following data.

--------------------Magnesium in $mmol_c.m^{-3}$-------------------------

	----------------------dilution-------------------------			
Magnesium standard	0.50->5.00	1.00->5.00	2.00->5.00	4.00->5.00
0.00 mg.L^{-1}	0	0	0	0
0.50 mg.L^{-1}	412	206	103	51
1.00 mg.L^{-1}	823	412	206	103
2.00 mg.L^{-1}	1650	823	412	206

B24: IRON by A.A.S.

Principle

Iron is measured with an A.A.S. at 248.3 nm wavelength and 0.2 nm slit. An oxidizing flame of air/acetylene (or N_2O/acetylene) is used. Organic acids interfere. Addition of 0.5% NaCl solution will overcome this problem. Iron shows a linear response in concentrations up to 5.0 mg.L^{-1} Fe.

Apparatus

A.A.S. (Perkin Elmer , type 560).
Acetylene gas (high quality).
Autosampler (Gilson, type 222).
Balance (0.01 g).
Infra-red lamp.
N_2O gas (high quality).
Vortex mixer.

Reagents

Hydrochloric acid 37% (HCl) p.a.
Iron ampoule (1.000 gram).
Sodium chloride (NaCl) p.a.

Hydrochloric acid (1 M).

Transfer 150 ml distilled water into a 250 ml beaker. Carefully add 20 ml HCl (37%). Cool and transfer to a 250 ml volumetric flask. Make up to volume with distilled water and homogenize. Store in a polypropylene bottle.

Sodium chloride (2.5 %).

Weigh 6.25 gram of NaCl (dried at 105° C) into a 250 ml beaker. Add 200 ml distilled water. Dissolve and transfer to a 250 ml volumetric flask. Make up to volume with distilled water and homogenize.

1.000 g.L^{-1} Iron stock solution.

Transfer quantitatively the contents of an iron ampoule, containing 1.000 gram of iron in HCl, into a 1 litre volumetric flask. Make up to 1 litre with distilled water and homogenize. Store in a glass bottle.

Standards

Pipette 5.00 ml iron stock solution into a 100 ml volumetric flask, containing 50 ml distilled water and 4 drops HCl (1 M). Make up to volume with distilled water and homogenize. Pipette from this solution respectively: 0.00, 5.00, and 10.0 ml into 50 ml volumetric flasks containing 20 ml distilled water and 3 drops HCl (1 M). Add 10 ml NaCl (2.5%) solution to blank and standards. Make up with distilled water and homogenize.

Blank:	0.00 mg.L^{-1} Fe
Standard 1:	5.00 mg.L^{-1} Fe
Standard 2:	10.0 mg.L^{-1} Fe

Procedure

Calibrate the instrument according to manufacturer's instructions and pipette (automatically) 4.00 ml sample and 1.00 ml NaCl (2.5%) solution into small tubes. Homogenize with a vortex mixer. Measure the samples, record the data and compare to the standards. Take artificially made samples to check analysis.

Remarks

- De-ionized water can be used

- Silica decreases the iron signal. Addition of 0.2 % $CaCl_2$ solution will eliminate this reduction. Normally no $CaCl_2$ solution addition is necessary.

- Viscosity effects (reduction of the iron signal) are observed by an excess of mineral acids.

- Iron stock solution must be kept in glass.

- Many interferences will be eliminated in a nitrous oxide flame, however sensitivity will be reduced.

- To prevent precipitation in the standard, 3 drops of HCl (1 M) are added instead of 1 drop.

- In case N_2O gas is used, an infra-red lamp is necessary to prevent freezing of the gas cylinder outlet.

- For our purposes, it is necessary to express the results in $mmol_c.m^{-3}$.
  By pipetting 4.00 ml sample to 5.00 ml final solution the standard series is:

Blank:	0 $mmol.m^{-3}$ Fe
Standard 1:	224 $mmol.m^{-3}$ Fe
Standard 2:	448 $mmol.m^{-3}$ Fe

Concentration can be read directly.

References

- Perkin Elmer Analytical Methods.

- Perkin Elmer Manual Instruction.

B25: IRON by AUTOANALYZER

Principle

Iron (II and III) are measured with an autoanalyzer system. A sample is mixed with potassium hydrogen phthalat. To this mixture hydroxyl ammonium chloride is added, after which iron (III) is reduced to iron (II). This iron (II) reacts with orthophenanthroline to give a red coloured complex at pH 3.5. Wavelength is 510 nm, flowcell is 10 mm.

Samples

Normally, acidified (pH 3-4) watersamples are used.

Apparatus

Autoanalyzer (Skalar, model 6000) + autosampler.
Balances (1 mg and 1 g).
Computer (+ interface).
Recorder.

Reagents

Brij-35 solution.
Iron ampoule (1.000 gram) p.a.
Hydrochloric acid 37% (HCl) p.a.
Hydroxyl ammonium chloride ($NH_2OH.HCl$) p.a.
1.10 Orthophenanthroline ($C_{12}H_9N_2Cl.H_2O$) p.a.
Potassium hydrogen phthalat ($KHC_8H_4O_4$) p.a.

Buffer solution.

Weigh 100 gram of $KHC_8H_4O_4$ in a 1 litre beaker. Add 600 ml distilled water. Dissolve. Transfer to a 1 litre volumetric flask. Make up to volume with distilled water. Add 1 ml Brij-35 solution and homogenize.

Hydroxyl ammonium chloride.

Weigh 25 gram of $NH_2OH.HCl$ into a 250 ml beaker. Dissolve in 150 ml distilled water. Transfer to a 250 ml volumetric flask. Make up to volume with distilled water and homogenize.

Orthophenanthroline reagent.

Weigh 625 mg of 1.10 $C_{12}H_9N_2Cl.H_2O$. Transfer to a 250 ml beaker. Dissolve in 150 ml distilled

water. Transfer to a 250 ml volumetric flask. Make up to volume with distilled water and homogenize.

Hydrochloric acid (1 M).

Add 20 ml HCl (37%) to 150 ml distilled water in a 250 ml beaker. Cool and transfer into a 250 ml volumetric flask. Make up to volume with distilled water and homogenize.

1.000 g.L^{-1} Iron stock solution.

Transfer quantitatively the contents of an iron ampoule, containing 1.000 gram iron in HCl to a 1 litre volumetric flask. Make up with distilled water and homogenize. Store in glass bottle.

Standards

Pipette 5.00 ml iron stock solution into a 500 ml volumetric flask, containing 300 ml distilled water and 4 drops HCl (1 M). Make up to volume with distilled water and homogenize. Pipette from this solution respectively:
0.00, 5.00, 10.0, 15.0, 20.0, and 25.0 ml into 50 ml volumetric flasks, containing a few mls distilled water and 3 drops HCl (1 M). The standards are respectively:

Blank: 0.00 mg.L^{-1} Fe
Standard 1:   1.00 mg.L^{-1} Fe
Standard 2:   2.00 mg.L^{-1} Fe
Standard 3:   3.00 mg.L^{-1} Fe
Standard 4:   4.00 mg.L^{-1} Fe
Standard 5:   5.00 mg.L^{-1} Fe

Procedure

Prepare the autosampler (figure 21) according to manufacturer's instructions. Fill sampler with standards and acidified samples. Run automatically at a speed of 60 samples per hour. Regularly run control samples and blanks to check the quality and baseline drift.

Remarks

-       To measure iron (II) only, replace NH$_2$OH.HCl solution with distilled water.

-       Rinse the system with HCl (1 M) for half an hour, followed by distilled water, before and after the analysis.

-       Before analysis, rinse all glassware with HCl (1 M). Iron can easily be absorbed on the wall of the glassware. Use acidified water between the samples.

- The speed of the analysis can be varied (up to 100 samples per hour). We prefer 60 samples per hour to have a better ratio between sample and rinse solution.
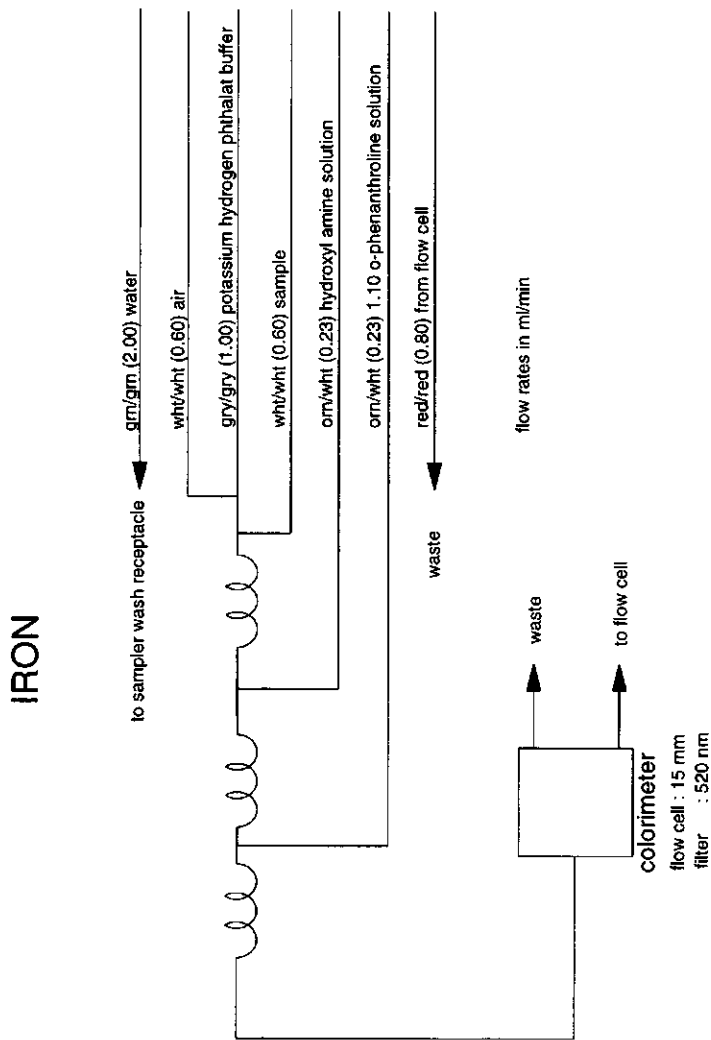
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- Burnichon, J., and J. Pre, 1974. Direct continuous flow automated determination of iron and iron binding capacity. Feuillets de Biologie 15(80):45-56.

- Caldwell, D.H., and R.B. Adams, 1946. Colorimetric determination of iron in water with 0-phenanthroline. Journal of the American Water Works Association 38:727.

- Skalar 6010/6000 Manual.

Appendix

For calculations of ionic balances, concentrations must be expressed as $mmol_c$. The above prepared standards correspond to respectively:

Blank:	0 $mmol_c.m^{-3}$Fe
Standard 1 :	35.7 $mmol_c.m^{-3}$Fe
Standard 2 :	71.4 $mmol_c.m^{-3}$Fe
Standard 3 :	107 $mmol_c.m^{-3}$Fe
Standard 4 :	143 $mmol_c.m^{-3}$Fe
Standard 5 :	179 $mmol_c.m^{-3}$Fe

Figure 21. Flow scheme for iron determination

IRON

to sampler wash receptacle

grn/grn (2.00) water

wht/wht (0.60) air

gry/gry (1.00) potassium hydrogen phthalat buffer

wht/wht (0.60) sample

orn/wht (0.23) hydroxyl amine solution

orn/wht (0.23) 1.10 o-phenanthroline solution

red/red (0.80) from flow cell

flow rates in ml/min

waste

colorimeter

flow cell : 15 mm
filter   : 520 nm

waste

to flow cell

B26: MANGANESE

Principle

Manganese is measured with an A.A.S. at 279.5 nm wavelength and 0.2 nm slit. An oxidizing flame of air/acetylene is used. The response of manganese is linear up to concentrations of 2.0 mg/l.

Samples

Watersamples are acidified (3 drops per 50 ml sample) before analysis.

Equipment

A.A.S. (Perkin Elmer, type 560).

Reagents

Hydrochloric acid 37% (HCl) p.a.
Manganese ampoule (1.000 g) p.a.

Hydrochloric acid (1 M).

Carefully add 20 ml HCl (37%) to 150 ml distilled water in a 400 ml beaker. Cool and transfer to a 250 ml volumetric flask. Make up to volume with distilled water and homogenize. Transfer to a 250 ml polypropylene bottle.

1.000 $g.L^{-1}$ manganese stock solution.

Transfer quantitatively the contents of a manganese ampoule, containing 1.000 gram of manganese in HCl, to a 1 litre volumetric flask. Make up to volume with distilled water and homogenize. Store in a polypropylene bottle.

Standards

Pipette 5.00 ml manganese stock solution into a 500 ml volumetric flask, containing 300 ml distilled water and 3 drops HCl (1 M). Make up to volume with distilled water and homogenize. Pipette from this solution respectively: 0.00, 10.0, and 20.0 ml into 50 ml volumetric flasks, containing 10 ml distilled water and 2 drops of HCl (1 M). Make up to volume with distilled water and homogenize.

Blank : 0.00 $mg.L^{-1}$ Mn
Standard 1 : 2.00 $mg.L^{-1}$ Mn
Standard 2 : 4.00 $mg.L^{-1}$ Mn

Procedure

Calibrate the instrument and measure the acidified samples against the standards. Follow manufacturer's instructions.

Remarks

- De-ionized water can be used.

- High concentrations of silica depress the manganese signal. This interference is overcome by the addition of $CaCl_2$ solution (0.2 %). Normally no addition of $CaCl_2$ solution is needed.

- High concentrations of iron (>10 g.L^{-1}) increases the manganese signal.

References

- Perkin Elmer Analytical Methods.

- Perkin Elmer Manual Instruction.

Appendix

For balance (sum cations and anions) studies, results are expressed as $mmol_c.m^{-3}$. Therefore we recalculate the standard concentrations and express them in $mmol_c.m^{-3}$ manganese. The above prepared standards correspond to respectively:

Blank :	0 $mmol_c.m^{-3}$ Mn
Standard 1:	73 $mmol_c.m^{-3}$ Mn
Standard 2:	146 $mmol_c.m^{-3}$ Mn

B27: "QUICKLY REACTIVE" ALUMINIUM

Principle

Different aluminium species react with oxine. The complex formed between aluminium and excess oxine, aluminium trioxinate, is extracted into chloroform, in which its concentration is measured spectrophotometrically at 390 nm. Reaction time is 2.3 seconds, pH is 5.0. This so-called quickly "reactive" aluminium fraction consists of Al^{3+}, its sulphatocomplexes, and mononuclear cationic hydrocomplexes. Fulvic and humic acid complexes, fluoride complexes and polynuclear aluminium species don't react with oxine at this pH and reaction time.

Equipment

Displacement bottle (Tecator).
Injector (6 port valve).
Magnet (teflon).
Membrane (Millipore, ϕ 13 mm, 0.2 µm flouropore) filter.
Peristaltic pump for tygon pump tubes (Technicon).
Reaction coils.
Recorder.
Sample-loop (250 µl).
Separator (see Clarke et al, 1992).
Spectrophotometer (Perkin Elmer, type 55).

Reagents

Aluminium ampoule 1.000 g p.a.
Acetic acid 100% (CH_3COOH) p.a.
Chloroform ($CHCl_3$) p.a.
Hydrochloric acid 37% (HCl) p.a.
Hydroxyl ammonium chloride ($NH_2OH.HCl$) p.a.
1.10 Ortho phenanthroline ($C_{12}H_9N_2Cl.H_2O$) p.a.
8-Hydroxyquinoline (oxine) (C_9H_7NO) p.a.
Sodium acetate (CH_3COONa) p.a.
Sodium hydroxide pellets (NaOH) p.a.

Hydrochloric acid (1 M).

Carefully add 20 ml HCl (37%) to 200 ml distilled water in a 400 ml beaker. Cool and transfer to a 250 ml volumetric flask. Make up to volume with distilled water and homogenize.

Sodium hydroxide (1 M) solution.

Pour 50 ml distilled water into a 250 ml beaker. Carefully add (heat development) 4 gram of NaOH pellets. Dissolve and cool. Transfer to a 100 ml volumetric flask. Make up to volume with distilled water and homogenize carefully.

Buffer solution.

Weigh 8.2 gram of sodium acetate and 34.74 gram of $NH_2OH.HCl$ in a 1 litre beaker. Add 800 ml distilled water. Add 2.35 gram of phenantroline and 1.0 gram of NaOH pellets. Dissolve. Add another 150 ml distilled water. Add NaOH (1 M) solution to pH 5.0. Transfer to a 1 litre volumetric flask. Make up to volume with distilled water and homogenize. Filter over a 0.45 μm filter.

Oxine solution.

Pour 400 ml distilled water into a 1 litre beaker. Add 1.5 ml HCl (1 M) solution and 200 μl acetic acid (100%). Add 0.581 gram of oxine. Dissolve by heating and stirring (teflon magnet). Add 0.541 gram of Na-acetate. Pour distilled water to approximately 950 ml volume. Adjust the solution to pH 5.0. Transfer to a 1 litre volumetric flask. Make up to volume and homogenize. Filter over a 0.45 μm filter.

Filling displacement bottle.

Pour approximately 50 ml distilled water into the displacement bottle. Then fill the bottle with $CHCl_3$ to the top. Close the bottle and tighten.

Phase separator.

Unscrew the phase separator. Place a new membrane in the middle of the separator and screw again. Don't tighten. Replace the separator in a horizontal position, because $CHCl_3$ has a higher density.

1.000 g.L^{-1} aluminium stock solution.

Transfer quantitatively an aluminium ampoule, containing 1.000 gram of aluminium to a 1 litre volumetric flask. Make up to volume with distilled water and homogenize.

Standards

Pour approximately 200 ml distilled water into a 250 ml volumetric flask. Add 5 drops HCl (1 M), swirl and pipette 25.0 ml aluminium stock solution. Make up to volume and homogenize. Pipette from this solution, respectively: 0.00, 1.00, 2.00, 3.00, 4.00, 5.00, and 10.0 ml into 200 ml volumetric flasks, containing 200 ml distilled water and 5 drops HCl (1 M). Make up to volume with distilled water. The standard series is now:

Blank:	0.00 mg.L^{-1} Al^{3+}
Standard 1:	0.50 mg.L^{-1} Al^{3+}
Standard 2:	1.00 mg.L^{-1} Al^{3+}
Standard 3:	1.50 mg.L^{-1} Al^{3+}
Standard 4:	2.00 mg.L^{-1} Al^{3+}
Standard 5:	2.50 mg.L^{-1} Al^{3+}
Standard 6:	5.00 mg.L^{-1} Al^{3+}

Procedure

Start the system by running distilled water for half an hour (figure 22). Watch the system carefully on leakage and a stable baseline pattern. Connect respectively buffer and oxine solution to the system. Again observe leakage and baseline stability. Inject a sample (inject by hand) in the system. Start the computer and measure the peak area. Run samples and standards. Compare peak area of standards and samples to calculate the results. Disconnect the oxine and buffer. Run for at least one hour. Preserve the organic waste.
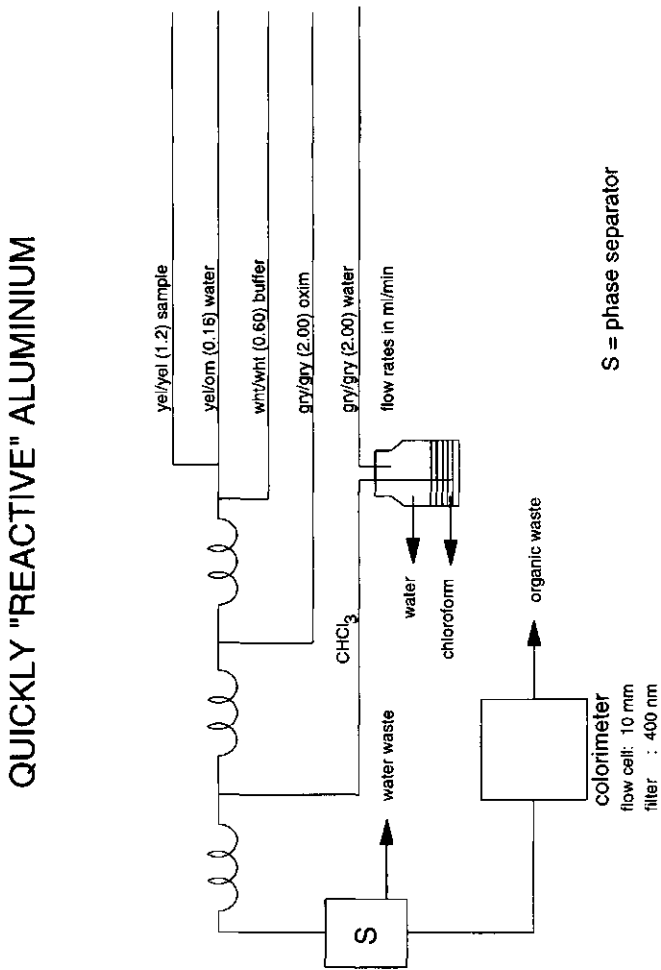
Remarks

-   The total procedure must be executed in a fume hood because of chloroform fumes. Be careful and take care of the organic waste. Use gloves.

-   To prevent toxic $CHCl_3$ fumes, the water phase is above the $CHCl_3$ phase, because of the higher density of $CHCl_3$.

-   In the phase separator, the membrane almost always causes leakage. Tighten the screws of the phase separator carefully. Replace the membrane before every sample series.

-   Because of the toxicity of the $CHCl_3$ and irregularities of the measurement, the injection is done by hand and not with an autosampler.

-   In most cases, "reactive" aluminium concentration is low. If necessary prepare a standard to 50 $mg.L^{-1}$ Al^{3+}.

-   The phase separator is the problematic part of the system. Check regularly for leakages. An instable baseline indicates membrane failure.

-   Aluminium (inorganic, monomeric Al^{3+}, sulphatocomplexes, and mononuclear cationic hydroxocomplexes) are included, fluoride complexes are excluded in the measurement.

-   Reaction time is critical.

-   Standard solutions must have a pH of about 2.5. At this pH, nearly all aluminium is present as Al^{3+}. The pH should not be lower, as the system cannot sufficiently buffer solutions below this value.

References

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Figure 22. Flow scheme for quickly "reactive" aluminium

QUICKLY "REACTIVE" ALUMINIUM

yel/yel (1.2) sample

yel/orn (0.16) water

wht/wht (0.60) buffer

grn/grn (2.00) oxim

grn/grn (2.00) water

flow rates in ml/min

CHCl$_3$

water

chloroform

organic waste

water waste

S

colorimeter
flow cell: 10 mm
filter : 400 nm

S = phase separator

ATOMIC ABSORPTION GRAPHITE TUBE FURNACE ANALYSIS

In the study of mineral weathering or cation exchange processes, low concentrations of elements may not be detectable with flame A.A.S. The latter technique is suitable in the $\mu g.ml^{-1}$ range, while the graphite tube furnace A.A.S. (GTA) can measure concentrations in the $ng.ml^{-1}$ range. Because the graphite tube furnace atomic absorption spectrometry technique is suitable for determining concentrations in the $ng.ml^{-1}$ range, this technique is eminently suitable for studies of soil solution dynamics. Another advantage of this technique is the low sample volume (max. 50 μl instead of mls) and the sensitivity (>100 times higher than flame absorption).

GTA measurements are normally executed in HCl (0.1 to 0.001 $mol.L^{-1}$). Because of the importance of the matrix effect, graphite furnace analyses cannot be standardized for a large range of samples. This matrix effect is far more important than in flame A.A.S. analyses and may highly influence the measurement. It often can be minimized by changing the appearance temperature or adding a modifier (e.g. palladium). Therefore each kind of sample matrix has its own analytical procedure. Nevertheless samples with only a small acid matrix can be analyzed satisfactory.

One of the major problems with GTA-AAS measurements is contamination. All precautions should be taken to minimize this. Dust-free rooms, freshly prepared ultra pure water, ultra pure chemicals, tested pipettes and pretreated (1 M HNO_3 rinsed) polypropylene volumetric flasks are the minimum conditions to determine low concentrations ($ng.ml^{-1}$).

Although we have carried out a large number of trace element analyses by GTA, in the following, we will restrict ourselves to the analysis of major elements.

B28: ALUMINIUM by GRAPHITE TUBE ATOMIZER (GTA)

Principle

Aluminium at low concentrations (ng.ml^{-1} Al) is measured with the graphite tube furnace technique. A sample is injected into a graphite furnace tube followed by drying, ashing and atomization. The obtained peak height or area is related to the amount of aluminium present. Concentrations are calculated by comparison with standards. Aluminium is measured at 309.3 nm wavelength, 0.5 nm spectral bandwidth and 10 mA lamp current.

Samples

Samples are acidified (HCl, 0.1 M or 0.001 M).

Apparatus

Finn pipette (0 - 5000 µL).
Graphite partition tubes.
UHQ water apparatus (milli-Q water).
Varian GTA 96 autosampler.
Varian Spectra AA 20 BQ plus.

Reagents

Aluminium ampoule p.a.
Hydrochloric acid 37% (HCl) suprapur.
Nitric acid 65% (HNO$_3$) suprapur.

Hydrochloric acid (0.1 M).

Pipette 2.0 ml HCl (37%) into a 250 ml polypropylene volumetric flask, containing 100 ml ultra pure water. Make up to volume with ultra pure water and homogenize.

Hydrochloric acid (0.001 M).

Pipette 2.0 ml HCl (0.1 M) into a 250 ml polypropylene volumetric flask, containing 100 ml ultra pure water. Make up to volume with ultra pure water and homogenize.

Nitric acid (0.1 M).

Carefully add 7 ml HNO$_3$ (65%) to 600 ml ultra pure water in a 1 litre volumetric flask. Make up to volume with ultra pure water and homogenize.

1.000 g.L^{-1} aluminium stock solution.

Transfer quantitatively the contents of an ampoule, containing 1.000 gram of aluminium, into a 1 litre polypropylene volumetric flask. Make up to volume with ultra pure water and homogenize.

Standards

Pipette 5.00 ml aluminium stock solution into a 50 ml polypropylene volumetric flask. Make up to volume with ultra pure water and homogenize (solution contains 100 µg.ml^{-1} Al). Pipette 2.00 ml from this solution into a 100 ml polypropylene volumetric flask. Make up to volume with ultra pure water and homogenize (2 µg.ml^{-1} Al). Pipette from this solution 1.00 ml into a 100 ml polypropylene volumetric flask. Make up to volume with HCl (0.1 or 0.001 M) and homogenize (20 ng.ml^{-1} Al). The aluminium standard series is pipetted from this solution.

The injection volume is 25 µl. The autosampler of the GTA-AAS automatically pipettes respectively: 0.00 µl, 5.00 µl, 10.0 µl, 15.0 µl, 20.0 µl, and 25.0 µl. The pipetted volume is filled up to 25 µl with HCl (0.1 or 0.001 M).

blank:	0 ng.ml^{-1} Al
standard 1:	4 ng.ml^{-1} Al
standard 2:	8 ng.ml^{-1} Al
standard 3:	12 ng.ml^{-1} Al
standard 4:	16 ng.ml^{-1} Al
standard 5:	20 ng.ml^{-1} Al

Procedure

Standards and samples are measured according to manufacturer's instructions. To get good results, samples and standards have to be measured in triplicate.

The following temperature program is used to measure aluminium.

step	temp. ° C	time sec.	gas flow L.min^{-1}	gas type	read command
1	85	5	3.0	normal	no
2	95	40	3.0	normal	no
3	120	10	3.0	normal	no
4	1000	5	3.0	normal	no
5	1000	1	3.0	normal	no
6	1000	2	0.0	normal	no
7	2500	1	0.0	normal	yes
8	2500	2	0.0	normal	yes
9	2500	2	3.0	normal	no

Remarks

- One of the major problems with AAS-GTA analyses is contamination. Therefore freshly prepared ultra pure water has to be used. Standards should always be prepared in the same volumetric flasks. All equipment has to be cleaned with HNO_3 (0.1 M). Volumetric flasks should be filled completely with acidified (HNO_3 0.1 M) ultra pure water when not used. Try to avoid glassware. Clean the furnace tube by running the temperature program without a sample. Sample cups must be kept in diluted HNO_3 (0.1 M).

- For our purposes no deuterium background correction and/or modifier is needed.

- In spite of less pure material we prefer to use aluminium ampoules instead of salts. Aluminium salts are often hygroscopic.

References

- Varian analytical methods.

- Varian manual instructions.

B29: SILICA by GRAPHITE TUBE ATOMIZER (GTA)

Principle

Small quantities of silica are measured by graphite tube furnace atomic absorption spectrophotometer (GTA-AAS). A sample is injected into a graphite furnace tube, followed by drying, ashing and atomization. The obtained peak height or area is related to the amount of silica present. Concentrations are calculated by comparison with standards. Silica is measured at 251.6 nm wavelength, 0.2 nm spectral bandwidth and 10 mA lamp current.

Samples

Samples are acidified with HCl (0.1 M or 0.001 M).

Apparatus

Finn pipette (0 - 5000 µl).
Graphite partition tubes.
UHQ apparatus (milli-Q water).
Varian GTA 96 autosampler.
Varian Spectra AA 20 BQ plus.

Reagents

Hydrochloric acid 37% (HCl) suprapur.
Silica ampoule p.a.
Nitric acid 65% (HNO_3) suprapur.

Hydrochloric acid (0.1 M).

Pipette 2.0 ml HCl (37%) into a 250 ml polypropylene volumetric flask, containing 100 ml ultra pure water. Make up to volume with ultra pure water and homogenize.

Hydrochloric acid (0.001 M).

Pipette 2.0 ml HCl (0.1 M) into a 250 ml polypropylene volumetric flask, containing 100 ml ultra pure water. Make up to volume with ultra pure water and homogenize.

Nitric acid (0.1 M).

Carefully add 7 ml HNO_3 (65%) to 600 ml ultra pure water in a 1 litre polypropylene volumetric flask. Make up to volume and homogenize.

1.000 g.L^{-1} silica stock solution.

Transfer quantitatively an ampoule, containing 1.000 gram of silica into a 1 litre polypropylene volumetric flask. Make up to volume with ultra pure water and homogenize.

Standards

Pipette 3.00 ml silica stock solution into a 200 ml polypropylene volumetric flask. Make up to volume with ultra pure water and homogenize (solution contains 15 μg.ml^{-1} Si). Pipette from this solution 1.00 ml into a 100 ml polypropylene volumetric flask. Make up to volume with HCl (0.1 or 0.001 M) and homogenize (150 ng.ml^{-1} Si). The silica standard series is prepared from this solution.

The injection volume is 25 μl. The autosampler of the GTA-AAS automatically pipettes respectively: 0.00 μl, 5.00 μl, 10.0 μl, 15.0 μl, 20.0 μl, and 25.0 μl. The pipetted volume is filled up to 25 μl with HCl (0.1 or 0.001 M).

blank:	0 ng.ml^{-1} Si
standard 1:	30 ng.ml^{-1} Si
standard 2:	60 ng.ml^{-1} Si
standard 3:	90 ng.ml^{-1} Si
standard 4:	120 ng.ml^{-1} Si
standard 5:	150 ng.ml^{-1} Si

Procedure

Standards and samples are measured automatically, following manufacturer's instructions. To get the best results, samples and standards have to be measured in triplicate.

The following temperature program is used to measure silica.

step	temp. ° C	time sec.	gas flow L.min^{-1}	gas type	read command
1	85	5	3.0	normal	no
2	95	40	3.0	normal	no
3	120	10	3.0	normal	no
4	900	5	3.0	normal	no
5	900	1	3.0	normal	no
6	900	2	0.0	normal	no
7	2700	1	0.0	normal	yes
8	2700	2	0.0	normal	yes
9	2700	2	3.0	normal	no

Remarks

-   To prepare a silica stock solution, it is difficult to weigh an exact quantity silica. Although the quality of the ampoule is less pure we prefer to use an ampoule.

References

-   Varian analytical methods.

-   Varian manual instructions.

B30: SODIUM by GRAPHITE TUBE ATOMIZER (GTA)

Principle

Low sodium concentrations are measured with the graphite tube furnace technique. A sample is injected into a graphite tube followed by drying, ashing and atomization. The obtained peak (height or area) of the sample is compared to standardpeaks. Concentration is calculated. Sodium is measured at 589.6 nm wavelength, 0.2 R nm spectral bandwidth and 5 mA lamp current.

Samples

Standards and samples have got a HCl (0.1 or 0.001 M) background.

Apparatus

Finn pipette (0 - 5000 µl).
Graphite partition tubes.
UHQ water apparatus (milli-Q water).
Varian Spectra AA 20 BQ plus.
Varian GTA 96 autosampler.

Reagents

Hydrochloric acid 37% (HCl) suprapur.
Nitric acid 65% (HNO_3) suprapur.
Sodium chloride (NaCl) suprapur, dried at 105°C.

> Hydrochloric acid (0.1 M).

Pipette 2.0 ml hydrochloric acid (37%) into a 250 ml polypropylene volumetric flask, containing 100 ml freshly prepared ultra pure water. Make up to volume with ultra pure water and homogenize.

> Hydrochloric acid (0.001 M).

Pipette 2.0 ml 0.1 M hydrochloric acid into a 250 ml polypropylene volumetric flask, containing 100 ml freshly prepared ultra pure water. Make up to volume with ultra pure water and homogenize.

> Nitric acid (0.1 M).

Carefully add 7 ml HNO_3 (65%) to 600 ml ultra pure water in a 1 litre polypropylene volumetric flask. Make up to volume with ultra pure water and homogenize.

1.000 g.L^{-1} sodium stock solution.

Weigh 0.6359 gram of NaCl (dried at 105°C). Transfer with freshly-prepared ultra pure water to a 250 ml polypropylene volumetric flask. Make up to volume with ultra pure water and homogenize.

Standards

Pipette 2.00 ml sodium stock solution into a 100 ml polypropylene volumetric flask. Make up to volume with ultra pure water and homogenize (solution contains 20 µg.ml^{-1} Na). Pipette 1.00 ml from this solution into a 100 ml polypropylene volumetric flask. Make up to volume with ultra pure water and homogenize (0.2 µg.ml^{-1} Na). Pipette 1.00 ml from this solution into a 100 ml polypropylene volumetric flask. Make up to volume with HCl (0.1 or 0.001 M) and homogenize (2 ng.ml^{-1} Na). This solution is used to prepare standards.

The sodium standard series is pipetted automatically from the 2.0 ng.ml^{-1} Na solution. The total injected volume is 25 µl. The autosampler of the GTA-AAS automatically pipettes respectively: 0.00 µl, 5.00 µl, 10.0 µl, 15.0 µl, 20.0 µl, and 25.0 µl. The pipetted volume is filled up to 25 µl with HCl (0.1 or 0.001 M).

blank:	0.0 ng.ml^{-1} Na
standard 1:	0.4 ng.ml^{-1} Na
standard 2:	0.8 ng.ml^{-1} Na
standard 3:	1.2 ng.ml^{-1} Na
standard 4:	1.6 ng.ml^{-1} Na
standard 5:	2.0 ng.ml^{-1} Na

Procedure

Standards and samples are measured automatically following manufacturer's instructions. To get good results, samples and standards have to be measured in triplicate.
The following temperature program is used to measure sodium.

step	temp. °C	time sec.	gas flow L.min^{-1}	gas type	read command
1	85	5	3.0	normal	no
2	95	40	3.0	normal	no
3	120	10	3.0	normal	no
4	700	5	3.0	normal	no
5	700	1	3.0	normal	no
6	700	2	0.0	normal	no
7	2000	1	0.0	normal	yes
8	2000	2	0.0	normal	yes
9	2000	2	3.0	normal	no

Remarks

-       The sodium stock solution is made from pure chemicals instead of an ampoule. Ampoules may be contaminated.

-       One of the major problems with AAS-GTA analyses is contamination. Therefore freshly prepared ultra pure water has to be used. Standards must always be prepared in the same volumetric flasks. All equipment has to be rinsed with HNO_3 (0.1 M). Volumetric flasks should be filled completely with acidified (HNO_3 0.1 M) ultra pure water when not used. Try to avoid glassware. Contamination in sample cups is a real problem. Therefore the cups should be *kept in acidified water. Before measurement clean the furnace tube by running* the temperature program without sample. Laboratory environment always contaminates.

-       For our purposes no deuterium background correction and/or modifier is needed.

-       Although the 589.0 nm line for sodium is more sensitive than the 589.6 nm line, the latter is recommended as it exhibits greater linearity.

-       A clean working environment is necessary to determine trace levels of sodium by graphite furnace AA, as the technique is extremely sensitive.

References

-       Varian analytical methods.

-       Varian instruction manual.

B31: POTASSIUM by GRAPHITE TUBE ATOMIZER (GTA)

Principle

Graphite furnace atomic absorption spectrometry is used for analyses of elements at low concentration range (ng.ml^{-1}). A sample is injected into a graphite tube followed by drying, ashing and atomization. In the atomization phase, free atoms produce an absorption signal. This peak height or area of the unknown sample can be compared to standards. Potassium is measured at 766.5 nm wavelength, 1.0 R nm spectral bandwidth and 5 mA lamp current.

Samples

The matrix of standards and samples is HCl (0.1 M to 0.001 M).

Apparatus

Finn pipette (0 - 5000 µl).
Graphite partition tubes.
UHQ water apparatus (milli-Q water).
Varian GTA 96 with autosampler.
Varian Spectra AA 20 BQ plus.

Reagents

Hydrochloric acid 37% (HCl) suprapur.
Nitric acid 65% (HNO$_3$) suprapur.
Potassium sulphate (K$_2$SO$_4$) suprapur, dried at 105°C.

Hydrochloric acid (0.1 M).

Pipette 2.00 ml HCl (37%) into a 250 ml polypropylene volumetric flask, containing 100 ml freshly prepared ultra pure water. Make up to volume with ultra pure water and homogenize.

Hydrochloric acid (0.001 M).

Pipette 2.00 ml HCl (0.1 M) into a 250 ml polypropylene volumetric flask, containing 100 ml freshly prepared ultra pure water. Make up to volume with ultra pure water and homogenize.

Nitric acid (0.1 M).

Carefully add 7 ml HNO$_3$ (65%) to 600 ml ultra pure water in a 1 litre polypropylene flask. Make up to volume with ultra pure water and homogenize.

1.000 g.L^{-1} potassium stock solution.

Weigh 0.5570 gram of K_2SO_4 (dried at 105°C). Transfer with freshly prepared ultra pure water to a 250 ml polypropylene volumetric flask. Make up to volume with ultra pure water and homogenize.

Standards

Pipette 1.00 ml potassium stock solution into a 100 ml polypropylene volumetric flask. Make up to volume with freshly prepared ultra pure water and homogenize (solution contains 10 µg.ml^{-1} K). Pipette 1.00 ml from this solution into another 1000 ml polypropylene volumetric flask. Make up to volume with freshly prepared ultra pure water and homogenize (0.1 µg.ml^{-1} K). Pipette 1.00 ml from this solution into a 100 ml polypropylene volumetric flask. Make up to volume with HCl (0.1 or 0.001 M) and homogenize (1 ng.ml^{-1} K). This solution is used for preparation of standards.

Normally, the injected volume is 25 µl. The autosampler of the AAS-GTA automatically pipettes respectively: 0.00 µl, 5.00 µl, 10.0 µl, 15.0 µl, 20.0 µl, and 25.0 µl from the 1 ng.ml^{-1} potassium solution. The pipetted volume is filled up to 25 µl with HCl (0.1 or 0.001 M).

blank:	0.0 ng.ml^{-1} K
standard 1:	0.2 ng.ml^{-1} K
standard 2 :	0.4 ng.ml^{-1} K
standard 3 :	0.6 ng.ml^{-1} K
standard 4 :	0.8 ng.ml^{-1} K
standard 5 :	1.0 ng.ml^{-1} K

Procedure

By following manufacturer's instructions, standards and samples are measured automatically. To get good results, samples and standards have to be measured in triplicate. The following temperature program is used.

step	temp. °C	time sec	gas flow L.min^{-1}	gas type	read command
1	85	5	3.0	normal	no
2	95	40	3.0	normal	no
3	120	10	3.0	normal	no
4	700	5	3.0	normal	no
5	700	1	3.0	normal	no
6	700	2	0.0	normal	no
7	2100	1	0.0	normal	yes
8	2100	2	0.0	normal	yes
9	2100	2	3.0	normal	no

Remarks

- The potassium stock solution is made from suprapur chemicals instead of an ampoule, because ampoules may be contaminated.

- One of the major problems with AAS-GTA analyses is contamination. Therefore freshly prepared ultra pure water has to be used. Standards should always be prepared in the same volumetric flasks. All equipment has to be cleaned with HNO_3 (0.1 M). Volumetric flasks should be filled completely, when not used. Try to avoid glassware. Standards should be prepared just before measurement. Even sample cups should be kept in HNO_3 (0.1 M) solution. Before measurement clean the graphite furnace tube by running temperature program without sample.

- Samples with this matrix do not need deuterium background correction and/or modifier.

References

- Varian analytical methods.

- Varian instruction manual.

B32: CALCIUM by GRAPHITE TUBE ATOMIZER (GTA)

Principle

Low calcium concentrations are measured using the graphite tube furnace technique. A sample is injected into a graphite furnace tube, followed by drying, ashing and atomization. The peak height or area is related to the amount of calcium present. Peaks are compared with standards to calculate the concentration. Calcium is measured at 422.7 nm wavelength, 0.5 R nm spectral bandwidth and 10 mA lamp current.

Samples

The matrix of the samples is HCl (0.1 M or 0.001 M).

Equipment

Finn pipette (0 - 5000 μl).
Graphite partition tubes.
UHQ water apparatus (milli-Q water).
Varian Spectra AA 20 BQ plus.
Varian GTA 96 autosampler.

Reagents

Calcium carbonate ($CaCO_3$) suprapur.
Hydrochloric acid 37% (HCl) suprapur.
Nitric acid 65% (HNO_3) suprapur.

Hydrochloric acid (0.1 M).

Pipette 2.00 ml HCl (37%) into a 250 ml polypropylene volumetric flask, containing 100 ml freshly prepared ultra pure water. Make up to volume with ultra pure water and homogenize.

Hydrochloric acid (0.001 M).

Pipette 2.00 ml HCl (0.1 M) into a 250 ml polypropylene volumetric flask, containing 100 ml freshly prepared ultra pure water. Make up to volume with ultra pure water and homogenize.

Nitric acid (0.1 M).

Carefully add 7 ml HNO_3 (65%) to 600 ml ultra pure water in a 1 litre polypropylene volumetric flask. Make up to volume with ultra pure water and homogenize.

1.000 g.L^{-1} calcium stock solution.

Weigh 0.6250 gram of CaCO^3 (dried at 105°C). Transfer to a 400 ml beaker. Carefully add 2.5 ml HCl (37%). Boil briefly. Cool and pour to a 250 ml polypropylene volumetric flask with ultra pure water. Make up to volume with ultra pure water and homogenize.

Standards

Pipette 5.00 ml calcium stock solution into a 100 ml polypropylene volumetric flask. Make up to volume with ultra pure water and homogenize (solution contains 50 µg.ml^{-1} Ca). Pipette 1.00 ml from this solution into a 100 ml polypropylene volumetric flask. Make up to volume with ultra pure water and homogenize (0.5 µg.ml-1 Ca). Pipette 1.00 ml from this solution into a 100 ml polypropylene volumetric flask. Make up to volume with HCl (0.1 or 0.001 M) and homogenize (5 ng.ml^{-1} Ca). This solution is used to prepare standards.

The calcium standard series is automatically pipetted from the 5.0 ng.ml^{-1} Ca solution. The total injection volume is 25 µl. The autosampler of the GTA-AAS automatically pipettes respectively: 0.00 µl, 5.00 µl, 10.0 µl, 15.0 µl, 20.0 µl, and 25.0 µl. The pipetted volume is filled up to 25 µl with HCl (0.1 or 0.001 M) .

blank:	0.0 ng.ml^{-1} Ca
standard 1 :	1.0 ng.ml^{-1} Ca
standard 2 :	2.0 ng.ml^{-1} Ca
standard 3 :	3.0 ng.ml^{-1} Ca
standard 4 :	4.0 ng.ml^{-1} Ca
standard 5 :	5.0 ng.ml^{-1} Ca

Procedure

Standards and samples are measured automatically, following manufacturer's instructions. To get good results, samples and standards have to be measured in triplicate. The following temperature program is used.

step	temp. °C	time sec.	gas flow L.min^{-1}	gas type	read command
1	85	5	3.0	normal	no
2	95	40	3.0	normal	no
3	120	10	3.0	normal	no
4	1000	5	3.0	normal	no
5	1000	1	3.0	normal	no
6	1000	2	0.0	normal	no
7	2600	1	0.0	normal	yes
8	2600	2	0.0	normal	yes
9	2600	2	3.0	normal	no

Remarks

- The calcium stock solution is made from pure chemicals (suprapur) instead of an ampoule, because ampoules are less pure.

- One of the major problems with AAS-GTA analyses are contaminations. Therefore freshly prepared ultra pure water has to be used. Standards should always be prepared in the same volumetric flasks. All equipment has to be cleaned with HNO_3 (0.1 M). Volumetric flasks should be filled completely with acidified ultra pure water when not used. Try to avoid glassware. Contamination in sample cups can appear and increase concentration. Clean the furnace tube before measurement by running temperature program without pipetting anything in the tube.

- For our purposes, no deuterium background correction and/or modifier is needed.

References

- Varian analytical methods.

- Varian instruction manual.

B33: MAGNESIUM by GRAPHITE TUBE ATOMIZER (GTA)

Principle

Magnesium at low concentrations is measured using the graphite tube furnace technique. A sample is injected into a graphite furnace tube followed by drying, ashing and atomization. The peak height or area is related to the amount of magnesium present. Peaks are compared to standards to calculate the concentration. Magnesium is measured at 285.2 nm wavelength, 0.5 R nm spectral bandwidth and 4 mA lamp current.

Samples

Samples are acidified with HCl (0.1 or 0.001 M).

Apparatus

Finn pipette (0 - 5000 µl).
Graphite partition tubes.
UHQ water apparatus (milli-Q water).
Varian Spectra AA 20 BQ plus.
Varian GTA 96 autosampler.

Reagents

Hydrochloric acid 37% (HCl) suprapur.
Magnesium sulphate ($MgSO_4.7H_2O$) suprapur.
Nitric acid 65% (HNO_3) suprapur.
Ultra pure (milli-Q) water (freshly prepared).

Hydrochloric acid (0.1 M).

Pipette 2.0 ml HCl (37%) into a 250 ml polypropylene volumetric flask, containing 100 ml ultra pure water. Make up to volume with ultra pure water and homogenize.

Hydrochloric acid (0.001 M).

Pipette 2.0 ml HCl (0.1 M) acid into a 250 ml polypropylene volumetric flask, containing 100 ml ultra pure water. Make up to volume with ultra pure water and homogenize.

Nitric acid (0.1 M).

Carefully add 7 ml HNO_3 (65%) to 600 ml ultra pure water in a 1 litre polypropylene volumetric flask. Make up to volume with ultra pure water and homogenize.

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1.000 g.L^{-1} magnesium stock solution.

Heat $MgSO_4.7H_2O$ in a crucible for a few hours at 700°C in a furnace. Cool in a dessicator. Weigh 1.2379 gram of $MgSO_4.0H_2O$. Transfer to a 250 ml polypropylene volumetric flask. Make up to volume with freshly prepared ultra pure water and homogenize.

Standards

Pipette 1.00 ml magnesium stock solution into a 500 ml polypropylene volumetric flask. Make up to volume with ultra pure water and homogenize (solution contains 2 μg.ml^{-1} Mg). Pipette 1.00 ml from this solution into a 100 ml polypropylene volumetric flask. Make up to volume with ultra pure water and homogenize (0.02 μg.ml^{-1} Mg). Pipette 1.00 ml from this solution into a 100 ml polypropylene volumetric flask. Make up to volume with HCl (0.1 M or 0.001 M) and homogenize (0.2 ng.ml^{-1} Mg). This solution is used to prepare the magnesium standard series.

The injection volume is 25 μl. The autosampler of the GTA-AAS automatically pipettes respectively: 0.00 μl, 5.00 μl, 10.0 μl, 15.0 μl, 20.0 μl, and 25.0 μl. The pipetted volume is filled up to 25 μl with HCl (0.1 or 0.001 M).

blank: 0.00 ng.ml^{-1} Mg
standard 1:   0.04 ng.ml^{-1} Mg
standard 2:   0.08 ng.ml^{-1} Mg
standard 3:   0.12 ng.ml^{-1} Mg
standard 4:   0.16 ng.ml^{-1} Mg
standard 5:   0.20 ng.ml^{-1} Mg

Procedure

Samples and standards are measured automatically, following manufacturer's instructions. To get good results, samples and standards should be measured in triplicate.
The following temperature program is used.

step	temp. °C	time sec.	gas flow L.min^{-1}	gas type	read command
1	85	5	3.0	normal	no
2	95	40	3.0	normal	no
3	120	10	3.0	normal	no
4	900	5	3.0	normal	no
5	900	1	3.0	normal	no
6	900	2	0.0	normal	no
7	2200	1	0.0	normal	yes
8	2200	2	0.0	normal	yes
9	2200	2	3.0	normal	no

Remarks

-    One of the major problems with GTA-AAS analyses is contamination. Therefore freshly prepared ultra pure water has to be used. Standards should always be prepared in the same volumetric flasks. All equipment has to be cleaned with HNO_3 (0.1 M). Volumetric flasks should be filled completely with acidified ultra pure water when not used. Try to avoid glassware. Contamination in sample cups can increase concentration. Clean the furnace tube by running the temperature program without a sample in the tube.

-    For our purposes, no deuterium background correction and/or modifier is needed.

-    The stock solution is made from suprapur chemicals instead of an ampoule (p.a. quality).

References

-    Varian analytical methods.

-    Varian instruction manual.

B34: SUM CATIONS AND SUM ANIONS

Introduction

Watersamples often originate from field monitoring programs. Researchers use the results for many purposes, for instance to acidification or weathering processes, or nutrition balance. An extra parameter that can be used is the balance of ions in solution, which, for laboratory staff, is a quality control of the analysis. Water samples are less tenable than, e.g., soil samples, because of microbial activity. In contrast to soil samples, certified material is hardly available. Quality control is therefore more difficult.

An often used method to check the quality of a water analysis is the comparison of the sums of cations and anions. A maximum difference of 5% between the sum of cations and that of anions is allowed. It gives an idea about the quality of the separate determinations. One should keep in mind that some cations or anions are not determined. We should therefore be careful to draw conclusions about the analytical quality when differences between the two sums are found. Nevertheless it is a useful indication.

Major cations are normally hydrogen, potassium, sodium, calcium, magnesium, aluminium, iron (Fe^{2+}), manganese (Mn^{2+}) and ammonium. The anions are chloride, nitrate, sulphate, phosphate and organic anions (SOA; see there).

To compare the results, concentrations should be expressed as $mmol_c$ or mol_c. Here results are expressed in $mmol_c.m^{-3}$.

To calculate the deviation between sum cations and sum anions the following formula is used:

(sum cations) - (sum anions) / ((sum cations + sum anions) / 2) * 100%

Reference

- Clesceri, L.S., A.E. Greenberg and R.R. Trussell, 1989. Standard Methods for the Examination of Water and Wastewater, 17th Edition, Published by A.P.H.A., A.W.W.A. and W.P.C.F., 20-21.

Section C

BULK DENSITY AND WATER RETENTION

by E.J. Velthorst

C. BULK DENSITY AND WATER RETENTION

Principle

A very important soil physics parameter is pF curve or water retention. It shows the relation between the volume fraction of the moisture content and soil water potential. Undisturbed core samples are used to determine the water content at low suction values. At higher suction, mass moisture ratio is not influenced by soil structure anymore. Therefore disturbed soil samples are taken. Water retention is expressed as volume percent water at a specific matric suction. The matrix suction is expressed as pF values (negative logarithm of the suction expressed in cm water) or in kiloPascal (kPa). 100 kPa equals 1 atmosphere pressure. In the following we will use pF values. Low pF values are obtained by means of a silt bath, high pF values with pressure plates and pans. At various suction values, in which the soil sample is equilibrated with its suction, water content is determined. The so-called pF curve can be made.

Moisture content between pF 0 and pF 2.0

- Before sampling weigh an empty 100 cm³ sample ring **(A g)**. This weight can also be obtained after measuring the water retention and cleaning the ring.
- Take an undisturbed soil sample by pressing the 100 cm³ ring vertically into the soil without disturbing soil structure. Avoid major cracks. Close the ring on both sides to avoid water loss.
- Remove both lids. Place the sample ring with sample on the silt bath. To avoid possible air explosion, slowly (one day) rise the water level from - 50 cm to the silt bath surface in small steps. Leave to saturate a few days. Cover the bath.
- Take the ring carefully off the silt bath. Clean and wipe off any water. Weigh **(B g)**. The sample is now saturated with water (pF 0).
- Place the ring on a silt bath again and set the waterlevel (pressure height) on - 10 cm (pF 1). Leave for about a week (cover the silt bath).
- Take the ring carefully off the silt bath. Clean and wipe off any water. Weigh **(C g)**.
- Repeat this step at -31.6 cm (pF 1.5) **(D g)**.
- Repeat this step at -100 cm (pF 2) **(E g)**.

Water content at pF 2.3 and pF 2.7

A high model pressure pan is used to determine the moisture content at pF 2.3 and pF 2.7 (20 and 50 kPa suction). Before analysis, the sample is pre-wetted on the silt bath again. Normally sandy soils are pressurized for one week and clayey soils for 2 weeks, before the pressure is released. Because the sample height is 5 cm, it is uncertain that all the water has been released. Because of the uncertainty of these results, one sometimes uses impractical water columns (- 200 cm and - 500 cm).

Procedure

- Fill the pressure pan (*high model*) with pre-wetted (saturated) plates.
- Connect the tubing inside the pan to the plates.
- Place a 100 cm^3 ring sample on the plates. Spray water drop-wise to ensure proper contact between sample and plate.
- Cover the pan and tighten screws. Be sure the equipment is in safe condition.
- If you only want to use the left hand side of the system (up to pF 3.4), close regulator 3 (see figure 23).
- Now the right hand side of the system is shut off.
- Close valve 10 (to the pan), followed by regulator 8 and 9 (manometer).
- Turn compressor on.
- Slowly open regulator 8.
- Open regulator 9 and adjust the manometer to the applied pressure (0.2 bar, pF 2.3)
- **Slowly** open valve 10. Re-adjust the pressure to 0.2 bar on the manometer with regulator 9.
- Leave for one or two weeks. Check the pressure twice a day.
- To stop the analysis, close valve 10 (pan). Close regulator 8 and switch off the compressor.
- Open the pan and remove the samples. Weigh immediately **(F g)**.
- Carefully open valve 10 and regulator 8 to release pressure.
- Repeat the same procedure. Now use 0.5 bar pressure (pF 2.7). Leave for another week. Weigh again **(G g)**.
- Place the sample ring in a drying oven and dry for at least 72 hours at 105°C. Weigh again **(H g)**.

Water content at pF 3.4

To measure the water content at pF 3.4 and pF 4.2, a 2 mm sieved disturbed sample is taken. Some sample is put into a porcelan dish, carefully wetted and sprayed with water, until a thin water layer is present. After 10 minutes the sample is saturated. Now the sample is ready to use for analysis.

- Fill the pressure pan (*high model*) with pre-wetted plates (pressure 3 bar).
- Connect the tubing inside the pan to the plates.
- Place special plastic rings (2.5 cm φ and 1 cm high) on the plate. Note ring number.
- Fill the ring with pre-treated (and wetted) sample with a spoon. Take care that the ring is completely filled. Be sure of optimal contact between plate and sample.
- Cover the pan and tighten the screws.
- If only the left hand side of the system (up to pF 3.4) is used, close regulator 3.

- Now the right hand side of the system is shut off.
- Close valve 10 (to the pan), followed by regulator 8 and 9 (manometer).
- Switch compressor on.
- Slowly open regulator 8.
- Open regulator 9 and adjust the manometer to the desired pressure (2.5 bar = pF 3.4)
- **SLOWLY** open valve 10. Re-adjust the pressure to 2.5 bar on the manometer with regulator 9.
- Leave for one week. Check the pressure twice a day.
- To stop the analysis, close valve 10 (pan). Close regulator 8 and switch off the compressor.
- Open the pan and remove the samples. Transfer the sample with a spoon to a pre-weighed **(J g)** crucible. Weigh the samples + crucible immediately **(K g)**.
- Carefully open valve 10 and regulator 8 to release pressure.
- Oven-dry the crucible with sample overnight at 105°C and weigh again **(L g)**.

Water content at pF 4.2

For pF 4.2 measurements in sandy samples the "*long* equipment route" can be chosen. For clay samples the "*short* equipment route" is recommended. The short route directly gives a quick and strong pressure; the long route is slow and gradual. The first 10 operations are the same for both methods.

1) Fill the pressure pan (*low model*) with other pre-wetted plates (pressure 15 bar).
2) Connect the tubing inside the pan to the plates.
3) Place special rings (2.5 cm ϕ and 1 cm high) on the plate. Note ring number.
4) Fill the ring properly with pre-treated (and wetted) sample. Make sure there is good contact between plate and sample.
5) Cover the pan and tighten. Don't forget the rubber ring. Be sure the equipment is safe.
6) If you only want to use the right hand side of the system (pF 4.2), close regulator 8 (see figure 23).
7) Now the left hand side of the system is shut off.
8) Close valve 7 (to the pan).
9) Close regulator 3.
10) Close regulator 6.

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Continuation for clayey samples (short procedure)

11a) Close valve 4 (manometer)
12a) Switch compressor on.
13a) Open regulator 3.
14a) Open valve 4 to adjust the manometer to the applied pressure (15 bar).

15a)   **SLOWLY** open valve 7. Re-adjust the pressure to 15 bar with valve 4.
16a)   Leave for one week. Regularly check the pressure.
17a)   To stop analysis, close valve 7 (pan). Close regulator 3 and switch off the compressor.
18a)   Weigh a crucible **(P g)**.
19a)   Open the pan and remove the samples. Bring over the sample material on the crucible. Weigh the samples + crucible immediately **(M g)**.
20a)   Carefully open valve 7 and regulator 3 to release pressure. If necessary, open regulator 6.
21a)   Place sample (+ crucible) in a drying-oven and dry for at least 72 hours at 105°C. Weigh **(N g)**.

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Continuation for sandy samples (long procedure)

11b)   Close valve 4.
12b)   Open regulator 6.
13b)   Close valve 5 (manometer).
14b)   Swith compressor on.
15b)   Open regulator 3.
16b)   Open valve 5 to adjust the manometer to the applied pressure (15 bar).
17b)   **SLOWLY** open valve 7. Re-adjust the pressure to 15 bar with valve 5.
18b)   Leave for one week. Regularly check the pressure.
19b)   To stop analysis, close valve 7 (pan). Close regulator 3 and switch off the compressor.
20b)   Weigh a crucible **(P g)**.
21b)   Open the pan and remove the samples. Transfer the sample material to the crucible. Weigh the samples + crucible immediately **(M g)**.
22b)   Carefully open valve 7 and regulator 3 to release pressure.
23b)   Place sample (+ crucible) in a drying-oven and dry for at least 72 hours at 105°C. Weigh **(N g)**.

Calculations

First calculate:

Oven-dry sample weight (pF 0 - 2.7)   **OD = H - A**

Then the moisture content (in wt%, w/w) at various pF values.

Moisture Content at various pF values.

pF 0.0 (1 cm or 0.001 bar or 0.1 kPa) = ((B - H)/OD) * 100 %

pF 1.0 (10 cm or 0.01 bar or 1 kPa)   = ((C - H)/OD) * 100 %

pF 1.5 (31.6 cm; 0.03 bar; 3.2 kPa) $= ((D - H)/OD) * 100 \%$

pF 2.0 (100 cm or 0.1 bar or 10 kPa) $= ((E - H)/OD) * 100 \%$

pF 2.3 (0.2 bar or 20 kPa) $= ((F - H)/OD) * 100 \%$

pF 2.7 (0.5 bar or 50 kPa) $= ((G - H)/OD) * 100 \%$

pF 3.4 (2.5 bar or 250 kPa) $= [\{(K-J)-(L-J)\}/(L-J)] * 100 \%$

pF 4.2 (15 bar or 1500 kPa) $= [\{(M-P)-(N-P)\}/(N-P)] * 100 \%$

The bulk density is obtained by:

$$\textbf{Bulk density (kg.dm}^{-3}) = \frac{OD}{\text{ring volume}} = \frac{OD}{100}$$

Conventionally, in pF curves the moisture content of the soil is expressed in volume % (w/v) rather than in weight % (w/w).

To convert wt % to vol % the following equation is used:

Moisture content (vol %) = moisture content (wt %) * bulk density.

Remarks

- Rubber tubing (inside the pan) connected to the plate gets a larger inner diameter during measurement. This results in lower pressure and inaccurate results. Use special tubing (manufacturer). Check the quality regularly.

- Use high pans for water content to pF 3.4. For higher pressure (pF 4.2) measurements, use low pans. A low pan (15 bar) use an extra rubber ring. Take care (safety aspect).

- Sometimes the outlet may bubble continuously. Probably the plate is defective. Replace.

- It is difficult to regulate both pans of the system at the time. I suggest to measure pF 3.4 and 4.2 separately.

- Pressure capacity is noted on the edge of the plate. Different plates are used for different pressure pans.

- Work safely with pressure pans, because of the high pressure. Only qualified persons are allowed to work with this equipment.

- Because of the uncertainty of the pF 2.3 and 2.7 measurements, they sometimes are not determined. Nowadays, computer programs are available to fit a pF curve without these 2 values. The other pF points are sufficient to get reliable curve.

- Sometimes samples are left in the laboratory for a few weeks. After that some sample is taken and dried at 105° C. This moisture content is used as pF 6 value. So another pF value is available to fit a pF curve.

Reference

- Van Reeuwijk, L.P., 1995. Procedures for Soil Analysis. ISRIC, Wageningen

Figure 23. pF high pressure equipment
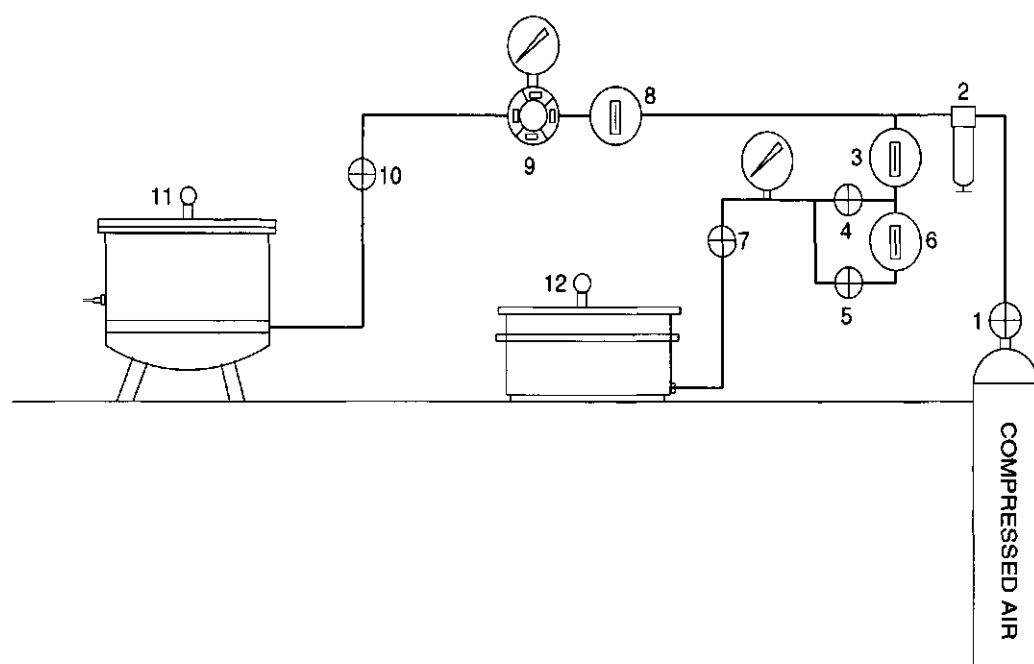
1:    tank with compressed air
2:    water filter
3:    pressure regulator
4:    valve
5:    valve
6:    fine pressure regulator
7:    valve
8:    pressure regulator
9:    fine pressure regulator
10:   valve
11:   extractor pan (low)
12:   extractor pan (high)

Section D

PARTICLE-SIZE ANALYSIS AND MINERALOGICAL ANALYSIS

by J.D.J. van Doesburg

D01. PRETREATMENT FOR GRAIN-SIZE AND MINERALOGICAL ANALYSIS

Introduction

The determination of the particle-size distribution of a soil, as well as the separation of the clay fraction (< 2 μm) and the separation of the heavy and light minerals, require that the particles are well dispersed in an aqueous solution, i.e. all aggregates have been disintegrated so that all individual particles are detached. In a few cases, this can be achieved by simply shaking the soil in water or by ultrasonic treatment of the soil suspension. In most cases, however, this will not give satisfactory results because of the presence of strongly cementing materials like carbonates, organic matter and iron oxides. Also, the presence of soluble salts may prevent a good dispersion due to the flocculating action of salts. So, pretreatment usually includes the removal of carbonates, if present, and the destruction of organic matter.

Whether the removal of iron oxides is desirable or not, depends on the sample, on the analyses which have to be executed and on the aim of the study. For X-ray diffraction analysis of the clay fraction, it has been the author's experience that removal of iron oxides is rarely necessary. On the other hand, removal of iron oxides is essential for the separation of the heavy and light minerals. Particles coated with iron oxides will not give satisfactory results. In addition, (electron) microscope examination of these coated particles will be difficult. For particle size analysis, the choice to remove iron oxides depends on the aim of the study.

Soluble salts are removed by dissolution in water. Because they are usually removed as a result of removal of carbonates or organic matter, no further attention will be given here to the removal of these salts.

After pretreatment, the samples are ready for further treatments, according to procedures for specific analyses, described in chapters C2-C4.

All procedures in this chapter are written for pretreatment of the soil sample for particle size analysis (pipette method). When pretreatment for particle size analysis by laser diffraction, for the separation of the clay fraction or for the separation of the heavy and light minerals are different, the reader is referred to the comments at the end of this chapter, indicated by a number between brackets in the text.

Apparatus

Balance (0.1 g accuracy)
Water baths
Centrifuge
Water jet pump

Removal of carbonates

Removal of carbonates with any acid will cause a very low pH which can cause destruction of small clay particles. To prevent this, a mild treatment with sodium acetate buffer solution (pH=5) is applied. When soils do not contain carbonates, which must be checked beforehand by adding one drop of 1N HCl to a small amount of soil and observing effervescence, the following procedure can be omitted. In that case, continue with the removal of organic matter.

Reagents

Sodium acetate buffer solution, 1M.
Acetic acid 100%.
Hydrochloric acid, 1M.
Magnesium chloride, 0.5N.
Hydrogen peroxide 35% (H_2O_2).

Sodium acetate buffer solution, 1M.

Dissolve 136 g. of sodium acetate ($NaC_2H_3O_2.3H_2O$) in about 950 ml of water. Adjust the pH to 5.0 with about 50 ml of acetic acid 100%. Control with a pH meter or "tritest" pH paper.

Hydrochloric acid, 1M.

Dilute 86 ml of concentrated HCl (37%) in about 900 ml of water and make up to 1 litre.

Magnesium chloride, 0.5N.

Dissolve 102 g. magnesium chloride ($MgCl_2.6H_2O$) in 1 litre water.

Procedure

1. Weigh 20 g. [1] of soil into a 800 ml beaker by taking small representative portions from several different parts of a well mixed soil sample that previously has been air-dried and ground to pass a 2 mm sieve.
2. Add about 50 ml of acetate buffer solution and place the beaker, covered with a watch glass, on a boiling water bath for about 30 minutes while stirring occasionally. (Don't forget to open the water-tap of the bath: due to evaporation, a constant small supply of water is needed to prevent the water bath from drying up!)
3. If the reaction has ceased, i.e. bubbles of CO_2 have stopped developing, about 5 ml of acetic acid (100%) is added. If there is no reaction, the carbonates have already been removed. If there is still a reaction, stir again occasionally until reaction ceases. Repeat adding small amounts of acetic acid until all carbonates have been removed. (Due to the low reaction rate of dolomite with acetic acid, removal of dolomite is much more time-consuming than that of calcite!)

4. To prevent the formation of insoluble calcium oxalate (oxalate may be one of the decomposition products after destruction of organic matter), the samples must be washed before H_2O_2 treatment. If possible (after standing overnight), first remove the clear supernatant liquid (including the floating roots) using a water jet pump, being careful not to lose any soil material. Then transfer the samples quantitatively to a centrifuge bottle of about 200 ml. Fill up the bottle with water (always use distilled or demi-water), balance pairs of bottles and centrifuge for about 15 minutes at 1800 rpm.

5. Decant the clear supernatant liquid or syphon it off. Fill the bottle half full with water, close it tightly with a rubber stop, and jar the soil loose from the walls by shaking vigorously. If the clay content is high, striking the bottom of the bottle on a large rubber stopper will probably facilitate redispersion. Clean the rubber stopper, fill the bottle with water again and centrifuge a second and last time for 15 minutes.

6. Decant the clear supernatant water. If some of the clay is still suspended, add a few drops of 1N HCl and, if necessary, 1N $MgCl_2$ to flocculate the clay and mix the supernatant without disturbing the sedimented material. After centrifuging, decant the clear supernatant. (If it is not clear again, add more HCl and $MgCl_2$ and repeat centrifuging)

7. The sample is now ready for removal of organic matter. Transfer the sample with a minimum of water back into the cleaned 800 ml beaker. If necessary, allow excess water to evaporate on a hot water bath until a volume of about 35 ml (=1 cm of liquid) has been reached.

Removal of organic matter

Hydrogen peroxide (H_2O_2) is used to oxidize the colloidal and humified organic matter and to disaggregate the soil particles. It is a strong oxidizing agent and therefore contact with the skin should be avoided. If contact is made, wash with water.

Efficient use of H_2O_2 requires an acid medium, which means that carbonates have to be removed first. The temperature should not exceed 75 °C because a higher temperature results in a rapid decomposition of H_2O_2, which should be avoided.

Reagents

Hydrogen peroxide (H_2O_2), 35%.
Magnesium chloride, 0.5M.
Ethyl alcohol (C_2H_5OH), 96%.

Magnesium chloride, 0.5M.

Dissolve 102 g. of magnesium chloride ($MgCl_2.6H_2O$) in 1 litre water.

Procedure

1. For samples which have not been treated before, weigh 20 g. [1] of soil into a beaker of 800 ml by taking small representative portions from several different parts of a well mixed sample that previously has been air-dried and ground to pass a 2 mm sieve, and add about 35 ml of water (use distilled or demi-water).

2. Together with the samples which have been treated previously for removal of carbonates, the beakers are placed on a cold water bath in a fume-cupboard. Add about 15 ml of H_2O_2 (35%) to each sample to give approximately a 10 % solution and cover the beakers with a watch glass.

3. The soil suspension is stirred occasionally and watched for about 30 minutes. If there is no strong reaction within that time, proceed with step 4. Particularly with soil samples rich in organic matter and/or manganese oxides, the reaction may proceed so rapidly that constant care and stirring is required to prevent frothing-over. Control reactions that are too vigorous by placing the beaker in cold water and, if necessary, by adding a few drops of alcohol. Continue adding small amounts of H_2O_2 until the sample ceases to froth.

4. Switch on the water bath, open the water-tap and slowly increase the temperature during the next few hours. Don't heat the samples over 75 °C! Because a strong reaction may still occur upon heating the samples, observe them closely until the samples have reached the maximum temperature. Stir occasionally.

5. When the reaction has ceased, repeat adding small amounts of H_2O_2 until the reaction is complete, i.e. the soil has lost its dark colour. Due to the decomposition of H_2O_2 in the presence of manganese oxides, a recurrent reaction after each addition need not indicate the presence of organic matter! Generally, three additions of 10-15 ml will be sufficient to remove all organic matter. Excess liquid (more than about 50 ml) can be evaporated by taking off the watch glass. Don't allow the sample to become dry!

6. After the removal of organic material is complete (fibrous material like roots cannot be removed with peroxide!), the excess of H_2O_2 is decomposed on a boiling water bath, stirring occasionally. Continue until the release of bubbles of oxygen has stopped. If necessary, let stand overnight at 80 °C.

7. To achieve a well-dispersed soil suspension, the sample has to be washed. If possible, first remove the clear supernatant (included the roots) using a water jet pump, being careful not to lose any soil material. Then transfer the sample quantitatively to a centrifuge bottle of about 200 ml, fill up with demineralized (demi) water, balance pairs of bottles and centrifuge for about 15 minutes at 1800 rpm.

8. Extract the clear liquid or decant, fill the bottle half full with water and stopper it tightly with a rubber stop. Jar the soil loose from the walls by shaking vigorously. If the clay content is high, striking the bottom of the bottle on a large rubber stop probably will increase dispersion. Short ultrasonic treatment can be used if necessary. Clean the rubber stop, fill up with water and centrifuge again. Repeat washing and centrifugation until the clay remains suspended. It may happen that there is only a relatively small amount of clay in suspension after the first or second washing procedure. Do not decant that clay, but try to flocculate it by adding a few drops of 1N HCl and, if necessary, 1N $MgCl_2$. Mix it without disturbing the sedimented material and centrifuge the sample for the last time. Alternatively, a longer centrifuging time may be applied.

Generally, the samples, freed of carbonates and/or organic matter, and washed, are ready for particle size analysis or the separation of the clay fraction. If removal of iron oxides is desired, as is nearly always the case for the separation of heavy and light minerals, continue with the following pretreatment.

Removal of iron oxides

The most successful method for removing iron oxides, without the destruction of small clay particles, is the sodium dithionite-citrate-bicarbonate (DCB) method described below. The method is based on the reduction of iron by sodium dithionite and the chelating or complexing action of citrate for ferrous and ferric iron. Sodium bicarbonate buffers the solution.

Reagents

Sodium citrate/bicarbonate solution.
Sodium dithionite ($Na_2S_2O_4$).
Sodium chloride solution, saturated.
Acetone (C_3H_6O), 99%.

Sodium citrate/bicarbonate solution.

Dissolve 88 g. (0.3M) of sodium citrate ($C_6H_5Na_3O_7.2H_2O$) and 8.4 g. (0.1M) of sodium bicarbonate ($NaHCO_3$) in 1 litre water.

Sodium chloride solution, saturated.

Dissolve 325 g. of sodium chloride (NaCl) in 1 litre water.

Procedure

1. Add 100 ml [2] of sodium citrate/bicarbonate solution to the samples [3] that previously have been treated for removal of carbonates or organic matter and jar the soil loose from the walls.
2. Warm the soil suspension to 75° C by placing the centrifuge bottles in the openings of a hot water bath. Avoid heating above 80° C because of the risk of forming insoluble FeS or elemental S.
3. Add about 2 g. [2] of sodium dithionite powder, using a spoon or spatula, and stir the suspension constantly for one minute and then occasionally during the next 10 minutes. Then add a second 2 g. portion of sodium dithionite and stir.
4. Take the bottles away from the water bath and observe the soil suspension. If the suspension fails to flocculate within 5 minutes, add 25 ml of a saturated NaCl solution and, if necessary, 10 ml of acetone. Mix the suspension and warm it to promote flocculation. Balance pairs of bottles and centrifuge for about 15 minutes at 1800 rpm [4].

5. Extract the clear supernatant liquid using a water jet pump or decant. Repeat steps 1 through 4 if a reddish-brown colour of the soil indicates that the removal of iron oxides is still incomplete.

6. After deferration is complete, wash the samples two or more times with water until the yellow-brown colour of the iron citrate complex has disappeared. If necessary for flocculation, wash with 1N NaCl and warm the suspension on a water bath before centrifuging.

7. After washing is complete, the sample, freed of carbonates, organic matter and iron oxides, is now ready for specific analyses.

Comments

[1] For particle-size analysis by laser diffraction only a very small quantity of sample will be used for measurement. Thus, if a representative small subsample can be taken, weigh less than 20 g. Generally, 5 g. will be sufficient for sandy soils as well as for clayey soils.
For clay separation, weigh proportionally more than 20 g. when dealing with soils with a low clay content, i.e highly calcareous or sandy soils.
For the separation of heavy minerals, weigh proportionally more than 20 g. for soils with a low content of sand (fraction >50 μm).

[2] For deferration of the sand fraction, take 50 ml of the citrate/bicarbonate solution and 1 gram of dithionite.

[3] For the separation of the heavy minerals, the fraction < 50 μm is not of interest. In that case, first remove the fraction < 50 μm by wet sieving.

[4] When dealing with the sand fraction only, centrifugation can be omitted. After mixing, wait about 20 seconds and decant being careful not too lose part of the sand fraction. The clay and silt particles which have been released by the deferration may be decanted at the same time.

D02. PARTICLE-SIZE ANALYSIS

Principle

After pretreatment of the soil for removal of cementing materials like carbonates, organic matter and, in some cases, iron oxides (see Chapter C1), the samples are ready for determination of the particle-size distribution. The particle-size distribution of a soil expresses the proportions of the various size classes, commonly represented by weight percentages of the total soil. A simple analysis comprises the determination of the fractions < 2 μm, 2-50 μm and > 50-2000 μm. If a more extensive analysis is desired, the silt and sand fractions can be subdivided in various size classes.

The method of particle-size analysis described here implies the quantitative separation of the sand fraction (> 50 μm) by wet sieving, and pipette sampling of the desired fractions < 50 μm, at fixed depths and times, upon sedimentation.

The pipette sampling method is based upon the relationship between the size of a spherical particle and its settling velocity in a viscous medium. This relationship, known as Stokes' law, says that

$$v = \frac{g \cdot D^2 \cdot (d_p - d_m)}{18.\eta}$$

where v is the settling velocity in cm/sec, g the gravity constant in cm/sec^2, D the diameter of the particle in cm, d_p and d_m the densities of the particle and the medium respectively in gm/cm^3 and η the coefficient of viscosity in gm/cm.sec or poises.

Since v = h / t (h = depth of fall and t = settling time), the settling time may easily be calculated by

$$t = \frac{18 \cdot \eta \cdot h}{g \cdot D^2 \cdot (d_p - d_m)}$$

The small volume of the suspension, taken by a pipette at a depth h after a settling time t, represents a sample from which all particles coarser than D μm have been eliminated, and in which all particles finer than that size are present in the same proportion as in the original sample. By weighing the soil particles in that specific volume, the percentage of particles < D μm can be calculated.

Apparatus

Ultrasonic processor
Balance (0.0001 g accuracy)
Water bath
Drying oven

Small 50 μm sieve
Sieving machine (including set of sieves 50-2000 μm)
Pipette sampling equipment

Reagents

Dispersing agent, 5%.

Dissolve 40.0 g (4%) of sodiumpolyphosphate $(NaPO_3)_6$ and 10.0 g (1%) of sodiumcarbonate (Na_2CO_3) in exactly (use volumetric flask) 1 litre water.

Dispersion and wet-sieving

Procedure

1. After pretreating the soil samples for removal of carbonates and organic matter (see Chapter C1), loosen the sediment in the centrifuge bottle by shaking with about 100 ml of demi-water and transfer the complete suspension to the cleaned 800 ml beaker you started with.
2. To disintegrate strongly aggregated particles and to achieve a well-dispersed soil suspension, the samples need ultrasonic treatment. Add 20 ml of dispersing agent, using a calibrated pipette and add water to bring the volume to about 350 ml. Immerse the probe of the ultrasonic processor about 1 cm into the suspension and start ultrasonic treatment during 5 min. with power output at 90%. (Alternatively, this treatment can also be applied directly to the soil in the centriguge bottle).
3. Put an appropriate funnel (Ø 10 cm) on a 1 l sedimentation cylinder. Inspect the small 50 μm sieve (Ø 8 cm) for cleanliness and possible damages, moisten both sides with water and place it on the funnel.
4. After ultrasonic treatment, decant the suspended portion of the soil suspension into the 50 μm sieve.
5. Add more water to the residue in the beaker, mix and allow to settle for about 30 seconds and decant the suspension as before. Repeat mixing and decanting several times until most of the silt and clay fraction has been passed through the sieve.
6. Now, transfer the complete sand fraction to the sieve by means of a jet of demi-water from a siphon, and wash the remaining silt and clay through the sieve until the separation of the coarse and fine fraction is complete (indicated by clear water coming through the sieve). Gentle brushing may be necessary. Afterwards, clean the brush above the sieve using some water.
7. Add water to bring the volume to 1 l and place the cylinder, covered with a watch glass, on the special sedimentation table. Prepare a blank cylinder by pipetting 20 ml of the dispersing agent into the cylinder and fill up to 1 l with demi-water. The samples are now ready for pipette sampling, described below. It is strongly advised to pipette the desired fractions within a few days: in spite of the presence of

dispersing agent, the chance of flocculation increases with time! Do not pipette before the fraction <50 µm obtained by sieving is added to the suspension.
8. Bring the sand fraction with some water to one side of the sieve and wash it quantitatively into a tared evaporating dish. Decant the clear water and evaporate the remaining water on a water bath.
9. Dry the samples for at least 2 hours in a drying oven at 105 °C. Then cool them in a desiccator and weigh to the nearest 0.001 g, giving the net weight of the fraction > 50 µm. Later on, the percentage is calculated on the basis of the total recovered sample. If further fractionation of the sand fraction is desired, proceed with sieving (see below).

Sieving the sand fraction (> 50 µm)

Procedure

1. Compose the desired set of sieves (Ø 20 cm), inspect them for cleanliness and damages, and arrange them on the bottom pan with the largest mesh size uppermost. (A commonly used set has the following mesh sizes: 1000 µm, 500 µm, 250 µm, 100 µm and 50 µm).
2. Transfer the sand fraction to the top sieve, place the cover and fasten the set firmly in the sieving machine.
3. Switch on the machine and sieve for 10 minutes with an amplitude of 8 and a medium interval.
4. Transfer the sieve fractions into tared weighing dishes by tapping each sieve upside down on the large metal funnel, placed above the dish. Weigh each fraction to the nearest 0.001 g and compare the cumulative weight of these fractions with the weight of the sand fraction you started with. Any material < 50 µm that has been collected in the bottom pan, is added to the suspension in the sedimentation cylinder. In case pipette sampling has already been done, this fraction (generally very small) is supposed to belong to the (coarse) silt fraction.

Pipetting fine fractions

Sampling by pipette sampling equipment requires many actions that have to be done in the right order. Without any experience, it is advised to acquire some practice by sampling water or an old suspension before sampling the suspensions that are to be measured. The numbers in the following procedure refer to Figure 24.

Procedure

1. Check if all taps are closed. If not, close them.
2. By turning the wheel at the right hand side, move the pipette downwards until the tip touches the water in the cylinder. Then set the ruler at the left side of the pipette to zero and fix it.
3. Now, turn the wheel until the tip of the pipette has reached the desired depth. The depth can be read on the ruler.
4. Open three-way-tap ❶, which is connected to the vacuum-pump, by turning it 90° clockwise.
5. After opening tap ❹, carefully open tap ❸ until the level of the suspension is just above tap ❸.
6. Close tap ❶ and ❹ and allow the sample above ❸ to flow away at **A** into any beaker by turning tap ❸ 90°. Clean this part of the pipette with some demi-water by turning tap ❷.
7. Allow the contents of the pipette to flow into a tared evaporating dish at **B** by opening tap ❸ and ❹. Clean the pipette with some water by opening tap ❷ and also allow this water to flow into the same dish.
8. Set all taps back into the original position and continue pipetting the next sample.
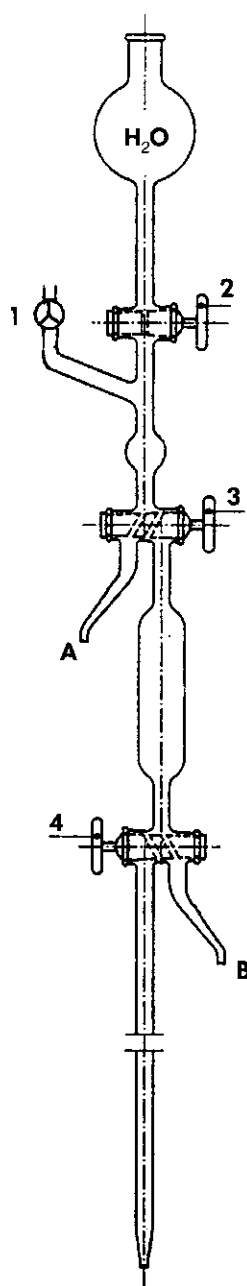
Determination of the total fraction < 50 µm

Before starting the sampling of the suspensions, two important issues should be discussed, i.e. the calibration of the pipette and the correction for the dispersing agent.

The pipette method is based on sampling a 20 ml volume from a 1 l suspension and so, a multiplication

Figure 24. Pipetting apparatus for suspended fractions.

factor of 50 (1000/20) is used in the calculations. To prevent errors, a well-calibrated pipette must be used at any time. Therefore, each new pipette has to be calibrated before use. In addition, recalibration of a pipette is necessary if it has not been used for a long period, or after cleaning. Calibration may be achieved by pipetting a volume of water (density at room temperature is 0.998 g/cm^3) into a tared bottle that can be closed to prevent evaporation. After weighing to the nearest 0.01 g, the volume of the pipette can be calculated. Repeat pipetting and weighing several times and calculate the mean value.

Because each sedimentation cylinder contains 1 g of dispersing agent (20 ml of a 5% solution), a correction should be applied in the calculations. In view of the importance of this correction, it is advised to prepare a blank cylinder by pipetting 20 ml of the dispersing agent and add water to 1 l. When sampling the suspensions, this blank must be sampled as well. The weight after drying at 105° C must be in agreement with the theoretical weight which depends on the concentration of the salt as well as the volume of the pipette.

Procedure

1. Close the first sedimentation cylinder with a rubber stopper and mix the suspensions thoroughly by end-over-end shaking. Make sure that all material from the bottom is mixed as well.
2. Put the cylinder on the table and immediately pipette 20 ml of the suspension at a depth of about 17 cm, i.e. the centre of the suspension. Transfer the contents of the pipette into a tared evaporating dish.
3. Repeat steps 1 and 2 for the other samples including the blank (in duplicate).
4. Put the dishes on a hot water bath, evaporate and dry for at least 2 hours in an oven at 105° C.
5. Remove the samples from the oven, cool them in a desiccator and weigh to the nearest 0.0001 g.

Determination of the fraction < 2 μm and other fine fractions

If silt fractions between 2 and 50 μm have to be determined (e.g., < 4, 8, 10, 16, 20 or 32 μm), the procedure for the determination of the < 2 μm fraction can be followed, but the depths and times should be adjusted according to Table 1. For any fraction not listed there, the time and depth may be calculated by using some convenient numbers from this Table. In that case, remember that the settling time is proportional to the depth of fall while it is inversely proportional to the square of the size of the particle.

Procedure

1. Record the temperature and stopper the first cylinder, mix well again and place it under the pipette assembly. Continue mixing the other samples every one or two minutes, depending on your experience with the pipette assembly.

Table 1. Depth (cm) at which fractions < 2 μm, < 8 μm and < 16 μm are pipetted as a function of temperature and sedimentation time.

Fraction Time	<2 μm 5½ hrs.	< 8 μm 30 min.	< 16 μm 10 min.		< 2 μm 5½ hrs.	< 8 μm 30 min.	< 16 μm 10 min.
Temp. °C				Temp. °C			
17	6.6	9.6	12.8	22	7.4	10.8	14.4
18	6.8	9.8	13.1	23	7.6	11.1	14.8
19	6.9	10.1	13.4	24	7.8	11.4	15.2
20	7.1	10.3	13.8	25	8.0	11.6	15.5
21	7.3	10.6	14.1	26	8.2	11.9	15.8

---

2. After sedimentation for 5½ hours, read the temperature again and use the mean of the two readings. Pipette at a depth according to Table 1 and transfer the contents of the pipette into a tared evaporating dish. Continue sampling the other suspensions every one or two minutes.

3. Evaporate the samples on a hot water bath, dry at 105° C for at least 2 hours, cool them in a desiccator and weigh to the nearest 0.0001 g.

Calculation of fractions

In the calculation model given here, we use the weight percentages of the following fractions: > 50 μm, 16 - 50 μm, 8 - 16 μm, 2 - 8 μm and < 2 μm

To obtain the weight percentages of these fractions, we first have to determine the weights (in grams, after drying at 105° C) of the different size fractions. Suppose

the weight of the fraction	> 50	μm =	**A**
the weight of V ml. of fract	< 50	μm =	**B**
"	< 16	μm =	**C**
"	< 8	μm =	**D**
"	< 2	μm =	**E**

the volume of the pipette (in ml.)	=	**V**
the weight of V ml. of the blank	=	**Z**

With the exception of the fraction > 50 μm, the weights of all pipetted fractions have to be corrected for the weight of the dispersing agent present in these fractions (**Z**). In addition, these corrected weights must be recalculated on basis of 1000 ml suspension by multiplying them with a factor of 1000/**V**.

This results in the following net weights

for the fraction	> 50 μm :		=	**A**
„	< 50 μm :	**(B - Z) . 1000/V**	=	**K**
„	< 16 μm :	**(C - Z) . 1000/V**	=	**L**
„	< 8 μm :	**(D - Z) . 1000/V**	=	**M**
„	< 2 μm :	**(E - Z) . 1000/V**	=	**N**
the weight of the complete sample:		**A + K**	=	**T**

The percentage of each size fraction can now be calculated by

% fraction	**> 50 μm**	=	**100 . A/T**
„	**16 - 50 μm**	=	**100 . (K-L)/T**
„	**8 - 16 μm**	=	**100 . (L-M)/T**
„	**2 - 8 μm**	=	**100 . (M-N/T**
„	**< 2 μm**	=	**100 . N/T**

In practice, these calculations should be automatized.

D03. SEPARATION OF THE CLAY FRACTION (< 2 µm)

Principle

For separation of particles below sieve size (≈ 50 µm) it is usual to employ a technique which depends on sedimentation laws. When a small spherical particle falls under the action of gravity through a viscous medium, it ultimately acquires a constant velocity. The rate of fall is governed mainly by the size of the particle and the difference in density between the particle and the medium. The relation is given by Stokes' law

$$v = \frac{g \cdot D^2 \cdot (d_p - d_m)}{18 \cdot \eta}$$

where v is the settling velocity in cm/sec, g the gravity constant in cm/sec^2, D the diameter of the particle in cm, d_p and d_m the densities of the particle and the medium respectively in gm/cm^3 and η the coefficient of viscosity in gm/cm.sec or poises. Although clay minerals are not spherical, the same equation is used to calculate the settling velocity of the clay fraction ($D < 2$ µm) of a soil by sedimentation in water.

To obtain the clay fraction, a well dispersed soil suspension must be mixed thoroughly and after a certain time (t sec) of sedimentation, all particles < 2 µm in the upper part (h cm) of the suspension can be drawn off by means of a siphon. At that time, all particles > 2 µm are below the level of h cm from the top of the suspension.

Since $v = h/t$ (h=depth of fall and t=settling time), the settling time may be calculated by using the following modified Stokes' equation:

$$t = \frac{18 \cdot \eta \cdot h}{g \cdot D^2 \cdot (d_p - d_m)}$$

From this equation, it can be seen that the settling time is proportional to the depth of fall and inversely proportional to the square of the diameter of the particle.

Although particle densities vary from one mineral to another, only an average density can be used. Generally, 2.65 g/cm^3 is taken.

Because the viscosity as well as the density of the medium are temperature-dependent, the settling time is temperature-dependent. For a range of temperatures that are encountered in the laboratory, the settling times for three different settling depths are given in Table 1. They may easily be recalculated for another depth of fall, density or particle diameter. Values for η and g can be found in the Handbook of Chemistry and Physics.

Apparatus

Ultrasonic processor

Reagents

Sodium hydroxide (NaOH), 1M.
Dissolve 40 g. of NaOH in 1 litre water.

Procedure

1. After pretreating the soil samples for removal of carbonates and organic matter (see Chapter C1), they are repeatedly washed by centrifuging until redispersion begins. To disintegrate strongly aggregated particles and to achieve a well-dispersed soil suspension, the samples need ultrasonic treatment.
2. Transfer the complete sample with some water into the cleaned 800 ml beaker you started with. Add demi-water to bring the volume to about 350 ml. Immerse the probe of the ultrasonic processor about 1 cm in the suspension and apply ultrasonic treatment during 5 min. with power output on 90%. (Alternatively, this treatment can also be applied directly to the soil in the centrifuge bottle).
3. Add water till about 1.5 cm below the rim of the beaker. To prevent flocculation and to obtain a stable well-dispersed soil suspension, adjust the pH to 7-8 (check with pH paper) by adding several drops of 1M NaOH. For a stable, well-dispersed suspension of allophanic soils, a much lower pH may be necessary.
4. Place the beakers close to the edge of the table (never in direct sunlight) leaving a distance of about 5 cm between beakers, and start stirring the first sample by using a stirring rod. Take good care that all soil particles at the bottom of the beaker are mixed as well. Write down the time you ended stirring the first sample and continue stirring the other samples for one minute each.
5. After stirring, cover the beakers with a watch glass and allow the particles to settle during the accorded time (Table 1). Take care that the samples are not disturbed in the meantime.

Table 1. Sedimentation times for separation of the clay fraction (< 2 μm) in water of different temperatures and with different settling depths, calculated on the basis of a particle size density of 2.65 gm/cm³.

			Settling depth			
	8 cm		9 cm		10 cm	
°C	hrs.	min.	hrs.	min.	hrs.	min.
17	6	41	7	31	8	21
18	6	31	7	20	8	9
19	6	21	7	9	7	57
20	6	12	6	58	7	44
21	6	3	6	48	7	33
22	5	55	6	39	7	23
23	5	46	6	29	7	12
24	5	38	6	20	7	2
25	5	31	6	12	6	53
26	5	24	6	4	6	44

6.   To collect the clay fraction, for each sample a polypropene 2 litre beaker is placed onto the draw-out table underneath the normal table. Fill some siphons, marked at 9 cm with tap-water using a clip to prevent them becoming empty.

7.   After the appropriate settling time, very carefully insert the siphon into the first soil suspension until the 9 cm mark has reached the surface of the suspension. Do not whirl up particles from the bottom part (if necessary practice first). Fix the siphon by inserting a piece of foam-rubber between the beaker and siphon. Open the siphon by removing the clip and allow the upper 9 cm of the suspension to flow into the 2 l beaker. Siphon off the following samples at the appropriate time.

8.   Repeat steps 3 to 7 once more. If, for some reason, the clay fraction has to be separated quantitatively, steps 3 to 7 must be repeated until the upper 9 cm of the suspension is clear after the selected settling time.

9.   Homogenize the collected clay fraction in the 2 liter beaker (be sure that there is no clay left at the bottom) and take out part of the suspension for X-ray diffraction analysis and store it in a polyethene bottle of 25, 50 or 100 ml, depending on the clay content of the soil. The remaining clay fraction is left in the beaker (covered with a watch glass) and saved until the clay mineral identification is finished. If this part of the clay fraction is used for, e.g., thermal analysis or chemical analysis, it should be (freeze) dried.

D04. SEPARATION OF HEAVY AND LIGHT MINERALS

Introduction

Heavy minerals are separated and concentrated to measure the total heavy fraction (e.g. for determination of weatherable minerals), and for further study of the fraction by petrographic microscope, X-ray diffraction, chemical analysis etc. Concentration of the heavy minerals greatly facilitates the study of these minerals because they generally make up only a small percentage of the sand fraction. In most soils that fraction is dominated by the light minerals quartz and feldspars.

Mineral separation using a heavy liquid is based on the difference in specific gravity of the minerals. After mixing the sand fraction with the heavy liquid, the light minerals will float on the liquid while the heavy minerals will sink to the bottom of the separating funnel where they can be drawn off. The light fraction can also be collected for further examination.

The heavy liquid used in our laboratory is bromoform. It has a density of 2.89 g.cm^{-3} and is easily diluted with organic solvents, such as N,N-dimethyl formamide, decaline, acetone, alcohols etc., to obtain a lower density, if necessary. Other widely used heavy liquids are tetrabromoethane (2.96 g.cm^{-3}) and diiodomethane (3.32 g.cm^{-3}).

To achieve a satisfactory separation of the heavy and light fraction, organic mattter, carbonates, and iron oxides have to be removed. Procedures are given in Chapter C1. After pretreatment, the desired particle size fraction has to be separated. For study of minerals by petrographic microscope, the fraction 50 - 420 µm is commonly used.

Apparatus

Special separation funnels with rack
Oven
Balance
Hot plate
Mounting needle
Tweezers

Reagents

Bromoform (CHBr$_3$), 96%, density $= 2.89$ g/cm^3.
Acetone (C$_3$H$_6$O), 99%.
Ethyl alcohol (C$_2$H$_5$OH), 96%.
Canada balsam.
Xylene (C$_8$H$_{10}$), 99%.

Mineral separation

1. After pretreatment of the soil sample for removal of carbonates, organic matter and iron oxides (chapter C1), the sample is sieved over a 50 μm sieve, after which the fraction > 50 μm is dried.
2. To obtain the fraction 50-420 μm, transfer the complete dry sand fraction into a clean 420 μm sieve and sieve (by hand) for some minutes. The fraction that passes through the sieve is used for heavy/light minerals separation.
3. Check the correct operation of the stopcocks of the separating funnels and put the funnels into the rack. Because of the toxicity of bromoform, the rack is placed in a fume-cupboard.
4. Close the stopcocks and fill the funnels with bromoform to about 2 cm below the rim.
5. Transfer the sand fraction to the funnel and mix it thoroughly with the bromoform using a glass rod. Cover the funnel with a watch glass and allow 30 minutes for the heavy minerals to settle.
6. Repeat mixing the sand fraction with bromoform every 30 min. without disturbing the sedimented fraction. Carefully mix the particles adhering to the walls. Continue until all heavy minerals have settled at the bottom of the funnel.
7. Put an appropriate tared porcelain dish below each funnel and release the heavy fraction by opening the stopcock for a very short time.
8. Wash the separated heavy fraction at least five times with a few ml. of acetone. Store the washings in a special bottle for recovery of the toxic and very expensive bromoform.
9. Dry the washed samples at 105 °C for about 30 min. and weigh them. The samples are now ready for further examination. For slide preparation, see below.
10. Place a conical flask (250 ml), provided with a normal funnel and coarse filter paper, below each separating funnel and filter the bromoform by opening the stopcock. To prevent becoming choked-up, close the stopcock just before the floating light minerals have reached the opening. The collected pure bromoform in the flask can be used again.
11. Wash the complete light fraction with some acetone into a porcelain dish and wash the fraction at least five times. Also wash the filter paper and store all washings for recovery of the bromoform.
12. If necessary, the light fraction may be dried, weighed and used for further examination.

Slide preparation

Because the separated fraction of heavy minerals may be very small, it is important to prevent loss of the sample. Hence, if you do not have any experience in making slides, it is advised to acquire some practice by preparing one or two irrelevant samples before preparation of the samples in question. All operations should be carried out in a fume-cupboard.

1. Place a microscopic slide (28x48 mm) that has been cleaned with some alcohol on the hot plate (about 125° C) and put a drop of Canada balsam in the centre, using a glass rod.
2. Take some sample with a microspatula and transfer the heavy mineral grains to the balsam, mix thoroughly with a mounting needle, and spread the paste uniformly so that an area of about 4 cm^2 is covered with grains that touch each other as little as possible.
3. The slide is left on the hot plate for a few minutes until the balsam has been cured; this may be ascertained by inserting the needle; the balsam attached to the needle should be tough within a few seconds.
4. Using tweezers, place a clean glass cover slip (24x24 mm), heated on the hot plate before, on the sample. To prevent air bubbles, put one side of the cover slip in the balsam and then slowly lower it. Air bubbles may be removed by gently pressing with the tweezers.
5. Remove the slide from the hot plate, let cool, and remove excess balsam by rubbing with a tissue moistened in xylene (toxic!).
6. The slide is now ready for mineral identification and counting by petrographic microscope.

Comments

Although the described heavy liquid separation is most effective for particles > 50 μm, separations may also be made for particles < 50 μm. In that case a centrifuge becomes necessary to accelerate the settling rates of the fine particles.

To perform separations in lower density ranges, halogenated heavy liquids may be diluted with a number of organic diluents. N,N-Dimethyl formamide (d = 0.945 g/cm^3) is one of the most suitable diluents because it has a low vapor pressure, like the heavy liquids, which results in a diluted solution with a stable density. Moreover, it has the advantage of being infinitely soluble in water so that recovery of the heavy liquid is very simple. Other organic solvents that can be used for dilution are benzene, decaline, acetone, alcohols etc.

Accurate measurement of the density of a liquid can be made by weighing a body with a known volume both in air as well as in the liquid. From the weight difference, the density of the liquid can be calculated. The actual density of a diluted heavy liquid may also be checked by using selected minerals with a known specific gravity or with an areometer.

Because heavy liquids are very expensive, while diluents are cheap, it is necessary to recover the heavy liquid from a diluted solution. The method used is based on the insoluble nature of the heavy liquid in water and high solubility in water of the diluent. After collecting all diluted bromoform in a five litre flask provided with a drain-cock, the diluent may be removed completely by allowing tap water to stream through the solution during a few hours. The purified heavy liquid at the bottom is then separated from the water and finally dehydrated by shaking with calcium chloride. After filtration, the density has to be checked.

All halogenated heavy liquids are light-sensitive and toxic. Therefore they should be stored in dark-coloured bottles while all operations must be carried out in a well-ventilated fume-cupboard.

Finally, it is worth mentioning that powdered sodium polytungstate, $3Na_2WO_4.9WO_3.H_2O$, may be used to prepare a heavy liquid by dissolving it in water. The main advantage is that it is nontoxic and that the density of a sodium polytungstate solution can be changed by adding either water or powdered salt. Diluted solutions may also be concentrated by evaporating part of the water on a water bath. The maximum density that can be attained is about 3.1 g/cm^3.

D05. SAMPLE PREPARATION FOR X-RAY DIFFRACTION ANALYSIS

Introduction

X-ray diffraction analysis is one of the most important techniques for the identification of minerals in soils and rocks. For the preparation of samples, various methods can be used that result in either (i) samples with parallel orientation of the particles, or (ii) randomly oriented specimens. The preferred method depends on the desired information. Generally, the identification of minerals asks for random orientation of particles, because only in that case the measured diffraction lines have the real relative intensities needed for a successful identification. On the other hand, the identification of clay minerals is best achieved using oriented clay specimens. Both methods of sample preparation for measurement by diffractometer will be described here. In addition, some attention is paid to the preparation of samples for the Guinier-camera.

Oriented specimens

The identification of clay minerals is best achieved by measuring their most diagnostic reflections, i.e. the basal reflections (00l). To enhance the intensities of these reflections, it is necessary to orient the clay minerals with their a-b axes parallel to the plane surface of the diffractometer. This automatically results in reduction of the intensities of the (hkl) reflections. Because most clay minerals have a platy morphology, orientation can usually be obtained easily.

Several methods may be used to orient the clay particles with the (00l) planes parallel to the sample holder. The most common are (i) sedimentation from suspension, under gravity or by centrifuging, on a microscope glass, (ii) smearing the clay paste on a glass slide, (iii) suction of suspended material onto a flat, unglazed, porous ceramic tile or cellulose membrane filter or (iv) making a tablet of the dry clay sample by applying high pressure.

The method which is employed in our laboratory, and which has proven to be very convenient, is the rapid suction of suspended clay onto a porous ceramic tile. The advantage of this method lies in the character of the ceramic material. After sedimentation, the clay can easily be saturated with different cations, necessary for identification, by simply percolating (by suction) the sediment with a 1 M chloride solution of the specific cation. The ceramic tile is unaffected by the heat treatments which are essential for identification of some clay minerals.

The routine identification of the clay minerals requires Mg^{2+}- and K^+-saturated specimens. After obtaining a diffraction pattern of both, the Mg^{2+}-saturated clay can be treated with glycerol, while the K^+-saturated clay can be used for various heat treatments.

Preparation

When preparing oriented clay specimens for a semi-quantitative estimate of the clay

mineral composition, two aspects are very important: 1) samples for X-ray diffraction should be mineralogically homogeneous throughout their thickness, and 2) the amount of clay deposited on the ceramic tile should be sufficient to insure that the intensities of the low and high angle peaks are not a function of specimen thickness. In other words, an "infinitely thick" sample should be employed. Apart from these aspects, the sample should be smooth, flat and long enough.

Apparatus

Suction equipment connected to a vacuum line (Figure 25).
Ceramic tiles (18 x 14 x 1.85 mm).
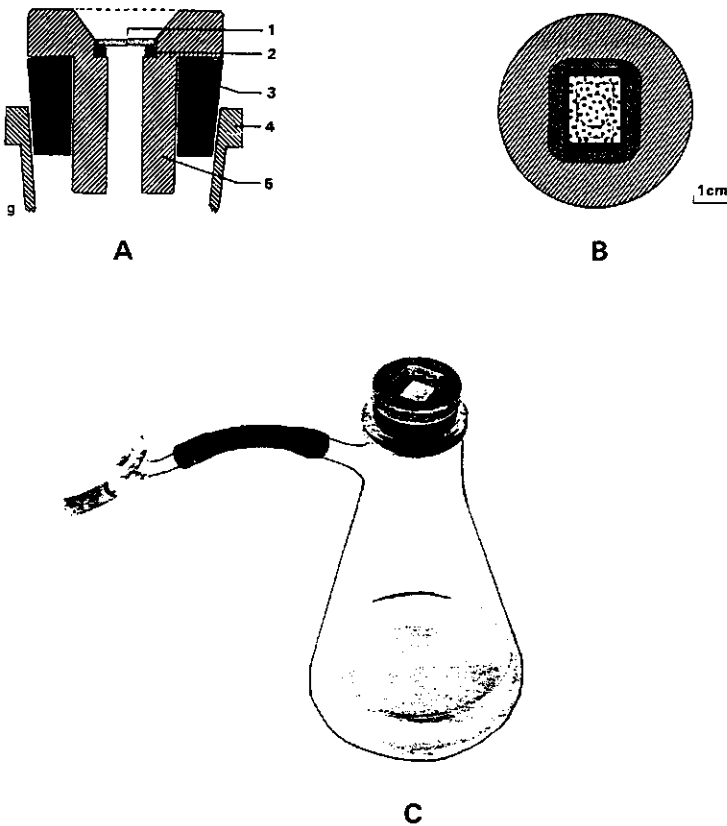
Figure 25. Suction equipment for preparation of oriented clay specimens on ceramic tiles.
A. vertical cross section upper part. 1: porous ceramic tile; 2. rubber waster; 3. perforated rubber stopper; 4. rim of vacuum flask; 5. stem.
B. upper part, view from above.
C. assembled unit, connected to vacuum line.

Reagents

Magnesium chloride, 0.5 M.
Potassium chloride, 1 M.

Magnesium chloride, 0.5 M.

Dissolve 102 g. of magnesium chloride ($MgCl_2.6H_2O$) in 1 litre water.

Potassium chloride, 1 M.

Dissolve 75 g. of potassium chloride (KCl) in 1 litre water.

Procedure

1. Write with a pencil the sample number and cation (Mg or K) on one side of the ceramic tile and place it upside down on the rubber of the suction device. Do this for all samples of a series.
2. Wet the tiles with some water and apply vacuum by turning the three-way tap 90° anti-clockwise.
3. Mix the separated clay fraction very thorougly and make sure that there is no clay left at the bottom of the container! To prepare a smooth and not too thick clay layer, a concentrated clay suspension should be diluted in a test tube: a suitable amount of suspension is obtained by dilution in a test tube until the light of a fluorescent lamp of the laboratory lighting is just visible through the suspension as a narrow line. This way, the amount of clay will never exceed the necessary quantity.
4. Pour the suspension in the suction device containing the correctly marked tile, and check if the filtrate is clear. If this is not the case, clean the suction device and/or take another tile and try again. If the filtrate is clear, repeat adding suspension until the clay layer on the tile is uniform of colour; the white colour of the tile should not shine through anymore.
5. Percolate with a solution of 0.5 M $MgCl_2$ or 1 M KCl during at least 45 minutes. Old salt solutions should be filtrated first, because some insoluble material may have been formed with time.
6. To prevent the formation of a salt crust on top of the clay film after drying, the excess of salt should be removed by percolation with a few ml. of demi-water (twice) after the last addition of the salt solution.
7. After washing with water, release the vacuum, take out the specimens with a spatula and place them on a piece of paper. Cover the tiles against dust and dry overnight at room temperature. The next day, the samples are ready for XRD analysis.

Comments

The most serious problem after sample preparation is the occasional curling, peeling and/or breaking up of the thin clay layer after drying. These imperfections not only lead to strongly reduced intensities of the important (00*l*) reflections, but also to incorrect d-spacings because the sample surface is no longer in the plane of the sample holder in the diffractometer. These imperfections may be caused by a variety of reasons. It is the author's experience that the most important causes are (i) the presence of much amorphous material, such as allophane or imogolite, (ii) the presence of a large amount of non-phyllosilicates such as quartz, cristobalite, tridymite, feldspar etc. and (iii) a too thick layer of clay, particularly when much smectite is present.

Several solutions to this problem are possible, e.g. (i) preparing another specimen with a (much) thinner clay layer, (ii) running the sample on the diffractometer just before it is completely dry, (iii) pressing a tablet of the powdered clay or (iv) removal of amorphous material by selective dissolution with acid (pH=3) ammonium oxalate. Deviation from the standard procedure, however, will usually produce poor diffraction patterns, except for the removal of amorphous material.

Randomly oriented specimens

Although the identification of clay minerals can best be achieved by their basal reflections, sometimes it is necessary to obtain the *hkl* reflections. If you are interested in the polytype of a clay mineral, for example 1M or 2M mica, or if you want to see the (060) reflection in order to distinguish dioctahedral from trioctahedral types, or if your study requires determination of the crystallinity, for example the Hinckley index of kaolinite, you want to see at least part of the *hkl* reflections. Such analyses will give good results only, when there is a perfectly random orientation of the clay particles, Because of the platy morphology of most clay minerals, however, a truly random orientation is difficult or impossible to achieve. The platy clay particles always tend to orient themselves parallel to the (00*l*) planes which should be avoided as much as possible.

Various procedures to prepare randomly-oriented specimens are described in literature. Some are simple, some elaborate, but no single method always gives the best results. Without going into details, the most important methods are (i) back-filling of the sample holder, (ii) filling from above by passing the sample through a sieve, (iii) spray-drying of the clay, (iv) embedding the clay in a thermoplastic cement, (v) sorption of clay onto flat polyester foam, (vi) mixing clay with powdered cork or (vii) side-filling of the sample holder. The method which is used in our laboratory and which is described in the next section, is the back-filling method. The advantage of this method lies in the fact that it is simple and fast, and gives satisfactory results.

Although the described method of sample preparation is particularly intended to prevent the orientation of clay minerals, it is good practice to apply the same method
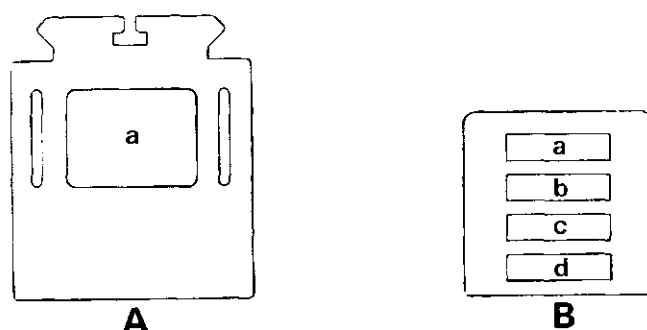
Figure 26. Specimen holders for XRD analysis. A. aluminium sample holder for diffractometry with cavity (a) for powder sample or ceramic tile.
B. metal sample holder for Guinier camera, with places (a-d) for powder samples.

for the identification of non-phyllosilicates. Besides clay minerals, there are many other minerals which have a platy or elongated morphology. Preparation of samples that contain such minerals may also lead to orientation of the particles, resulting in enhancement and weakening of specific reflections. Without real relative intensities of diffraction lines, however, the identification of such minerals may become difficult or even impossible.

Preparation

If the sample holder (Figure 26A) is packed from above, final pressing of the powder by a flat surface or any shear motion on the surface, will enhance the undesirable orientation of the minerals. To avoid this as much as possible, the sample holder should be packed from the back. The applied method of sample preparation only requires an aluminium sample holder with a removable bottom and abrasive paper No. 320. The powdered clay sample may be obtained by drying the separated clay suspension on a water bath or by freeze drying. All other samples should be ground to a very fine powder in an agate mortar.

Procedure

1. The abrasive paper is laid down onto the table with the rough surface upwards.
2. After removing the bottom of the aluminium sample holder by simply pushing it out, the holder is laid down on the abrasive paper.
3. While pushing down the sample holder, a spatula is used to tamp the powder evenly into all parts of the sample holder cavity. Gently press the powder straight down into the cavity until it is filled completely.
4. Carefully scrape all powder from the sample holder surface and replace the metal bottom again.

5. Turn the sample holder upside down very carefully and make sure that the cavity is filled evenly and the surface of the powder is on level with the surface of the sample holder. If so, the sample is ready for XRD analysis.

Comments

The ultimate result of preparation of samples as described above, is dependent on several factors, such as, (i) the applied pressure, (ii) clay or non-clay material, (iii) the grain size of the material and (iv) the grain of the abrasive paper. It may happen that the powder is too loosely packed, which results in loss of powder when turning over the sample holder. More pressure has to be applied then or, when dealing with non-clay material, the powder is not ground fine enough. When the powder is sticking to the abrasive paper, less pressure or abrasive paper with a finer grain size has to be used. The use of rough filter paper may be a good alternative. The preparation of randomly oriented specimens sometimes asks for some flexibility on the part of the operator.

Preparation of specimens for the Guinier-camera

Although the diffractometer is unmistakably the best choice for identifying clay minerals, the Guinier-camera is equally useful, or even better, for the identification of non-phyllosilicates. Some advantages of the Guinier-camera are a better resolution of the diffraction lines, no quantity of chart paper when comparing patterns of various samples, the possibility to record the diffraction pattern of three samples at the same time, and the small quantity of sample required to make a diffraction pattern. A serious disadvantage of the Guinier-camera is related to the measurement of intensities. They have to be estimated from the blackening of lines on the film, whereas they can be measured directly by using a diffractometer.

After grinding the sample to a very fine powder, the specimens can easily be prepared by simply mixing the sample with a drop of glycerol. Smearing the paste on a special sample holder generally results in a randomly oriented specimen.

Procedure

1. Take a small, but representative part of the sample to be analyzed. Put it in a clean, small ($\varnothing \approx 4$ cm) agate mortar, and grind it with an agate pestle until all gritty feeling has disappeared (too coarse samples give spotty diffraction lines.)
2. Put a small drop of glycerol on the rim of the mortar and take some glycerol on top of a small spatula and mix it with the powdered sample. Add more glycerol, if necessary, and mix until enough well-spreadable paste has been made.

3. Place a clean sample holder (see Fig. 26B), with the foil upwards, on the table and take some of the paste on the back of the cleaned spatula and spread the paste evenly on the upper position (a) of the sample holder.
4. Prepare a second and a third sample for the positions b and c respectively. Be careful not to mix with the adjacent sample. The lowest or fourth position (d) on the sample holder will not be used.
5. After completing the special card for administration whereupon the registration of film number, radiation, film type, exposure time, adhesive, date, signature and the description of the samples, a Guinier exposure can be made.

Section E

SAMPLE PREPARATION FOR
X-RAY FLUORESCENCE ANALYSIS

by A.J. Kuijper

Principle

X-Ray Fluorescence Spectrometry today is widely accepted as a versatile method of instrumental element analysis. XRFS-analysis is fast, non-destructive and accurate.

In the XRF-spectrometer, the sample is irradiated by an X-ray beam consisting of a broad band of continuous radiation. In return, the chemical elements present in the sample produce secondary (fluorescent) X-rays. These secondary X-rays are characteristic for each specific element. The intensity of the secondary radiation is proportional to the concentration of the element. In this way the concentrations of all elements of interest can be calculated by measuring the intensity of the secondary radiation.

XRFS can handle a great variety of sample types: liquids, powders, solids, plant-tissue, metals, clay, soil or rock. In the XRF-laboratory of the Department of Soil Science and Geology, the procedures and equipment are optimized for the analysis of clay, soil and rock samples. The analysis is performed with a Philips wavelength-dispersive spectrometer PW1404.

Basically there are two methods for sample preparation: borate-disk and pressed tablet. Borate-disks, compared to pressed tablets, have the main advantage that effects of particle size and mineralogy are eliminated, while inter-element effects are minimized. A disadvantage is the (high) dilution. This can be a problem for the analysis of trace elements with low concentrations (< 20 ppm). Therefore, we use borate-disk for routine quantitative analysis of major, minor and trace elements, while the pressed tablet is used for qualitative analysis or for quantitative analysis of volatile components or trace elements. This manual includes the procedures for both sample-preparation methods.

The samples are measured according to apparatus' instructions and radiation-safety regulations.

Sample pre-treatment

Principle

Usually, a laboratory sample is air-dried and sieved over a 2mm sieve (fine earth fraction). If the sample contains particles > 2 mm that should be included in the XRFS-analysis, the sample has to be crushed with a crushing machine to obtain a sample with particle size < 2 mm.
If the clay fraction of a sample has to be analyzed with XRFS, it has to be separated first (see Section D). After separation, the clay fraction is freeze-dried prior to further treatment.

For XRFS-analysis, it is essential that the sample material is finely ground to a particle size of < 25 μm. Depending on the selected preparation method the ground sample has to be dried (105° C; pressed tablet, if used for quantitative analysis) or dried (105° C) and ignited (900° C; borate-disk).
Borate-disks are prepared with ignited sample material and therefore the loss on ignition has to be determined. As the results of XRFS-analysis are to be calculated on the basis of oven-dry sample, the concentrations measured in borate-disks should be corrected for loss on ignition. For further details on sample pre-treatment see Chapters A2 and A3.

Chemicals used in the procedures for sample pre-treatment and preparation should be of analytical grade. Special attention should be given to avoiding contamination during sample pre-treatment and preparation as well as surface contamination of the prepared borate-disk or pressed tablet (do not touch with your fingers!).

<u>Apparatus</u>

Crushing machine
Sample splitter
End-over-end shaker
Agate mortar and pestle
Ball mill
Porcelain crucibles
Drying oven
Ignition oven
Desiccator

<u>Procedure</u>

Crushing

Prior to crushing, check whether the sample-chamber, the crushing blades and the sample-collector are clean. Check whether the sample-collector is properly installed.
The air-dried field sample is transferred to the sample chamber of the crushing machine. After crushing, the sample-material should be thoroughly mixed, split and mixed again to give a homogeneous laboratory sample.

Grinding

-       Select the grinding device which suits best your analytical needs, depending on the type of sample material and the range of elements of interest (see Table 1).

Table 1. Grinding devices

Material	Density / Hardness	Sample weight (max.)	(possible) Contamination
Syalon	3.3 / 9	10 g.	**Y** Si Al
Tungsten-carbide	13.5 / 8.5	2 g.	**Co W**
Agate	2.2 / 7.5	10 g.	Si
Corundum	3.6 / 9	2 g.	**Al**

- Fill the grinding vessel or mortar with a small part of the sample material. Grind the sub-sample for a few minutes. Remove the ground material (which may be contaminated by material of a previous sample) and clean the vessel with tissue.
- Fill the grinding vessel with the sample material. Grind the sample for about 3-5 minutes.
- Check whether the sample is fine enough. If necessary, repeat grinding.
- Clean the vessel by grinding some quartz-sand for a few minutes.

Drying

- Weigh an empty crucible (**weight A**, accuracy 1 mg). Add about 1.5 g of sample.
- If moisture content has to be determined, weigh the crucible again (**weight B**). Dry the crucible + sample overnight in a drying oven at 105° C, transfer to a desiccator and weigh again after cooling to room temperature (**weight C**; compare Chapter A4, moisture content).

- If total sulphur is to be determined, the sample has to be pre-oxidized with excess of ammoniumnitrate (NH_4NO_3), as follows:
Add about 1g. ammoniumnitrate. Mix carefully. Add as much water as necessary to moisten the mixture and mix again. Clean the spoon carefully with a little water. Place the crucible overnight in the drying oven (105°C).

Ignition

After drying, place the crucible in the ignition oven and allow the sample to warm up gradually to 900° C. Ignite for at least four hours. Allow the oven to cool down (ca. 100° C). Transfer the crucible to the desiccator and allow to cool to room temperature. Finally weigh the crucible again (**weight D**). Calculate the loss on ignition (L.o.I.).

Calculation of L.o.I.:

$$\text{L.o.I.} = \frac{(\text{C - D})}{(\text{C - A})} \times 100\%$$

Sample preparation for borate-fusion

Principle

The ignited sample is mixed with glass-forming lithium tetraborate and fused in a high frequency fusion machine. By fusion, the sample is homogeneously dissolved in the borate-flux. After cooling/casting, a so-called "solid solution" is formed. The borate-disk can be analyzed by XRFS.

Apparatus

Agate mortar and pestle
Fusion machine
Platin/gold 95/5 crucibles

Chemicals

Lithium-tetraborate $Li_2B_4O_7$
Lithium iodide (LiI) solution (saturated in acetone)

Procedure

-       After ignition of the sample, homogenize and grind again, if necessary, in the mortar. Carefully weigh 2400.0 mg of oven-dry (50° C) lithium tetraborate. Add 600.0 mg of sample (accuracy 0.1 mg). Carefully mix sample and flux in the mortar.
-       Transfer the mixture to a flat-bottomed Pt/Au crucible. Add 4 to 5 drops of LiI-solution as a non-wetting agent.
-       Transfer the crucible to the high-frequency fusion machine.
        The fusion machine is pre-programmed for power and fusion time according to apparatus' instructions.
-       Start the fusion machine to allow the mixture to melt. After cooling, solidification and casting, the flat lower surface of the disk is used for XFRS analysis.

Preparation of pressed tablets

Principle

The sample is mixed with organic WAX and pressed to give a compact tablet. The flat lower surface of the tablet is used for XRFS analysis.
The main advantage of the pressed tablet, as compared to the borate-disk, is that dilution of the sample is reduced. Special attention should be given to effects of mineralogy and particle-size. The pressed tablet can be used for qualitative analysis or quantitative analysis of volatile components and trace elements.

Apparatus

Agate mortar and pestle
Mylar foil
Pressing cylinder
Pressing machine

Chemicals

Hoechst WAX-C (Ethylenbistearoylamid $H_{35}C_{17}CONHC_2H_4NHCOC_{17}H_{35}$)

Procedure

- Accurately weigh the required amount of WAX in a plastic vessel.
- Add 2000.0 mg of finely-ground, oven-dry (105° C) sample (accuracy 0.1mg).
- Close the vessel and thoroughly shake for a few minutes. Transfer the mixture to the mortar and carefully mix again.
- Cover the base of the pressing unit with a piece of Mylar foil. Place the pressing cilinder on top of the base.
- Carefully put the mixture in the cilinder. Take care that the bottom is equally covered by the mixture. Place the pestle in the cilinder. Place the unit in the pressing machine and press at 250kg/cm^2 for 10 seconds.
- Take out the unit and gently remove the cilinder. Take out the pressed tablet carefully. The bottom surface of the tablet can be analyzed by XRFS for elemental composition.

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SAMPLE PREPARATION FOR GRAIN-SIZE DETERMINATION BY LASER DIFFRACTION

by Th. Pape

F. SAMPLE PREPARATION FOR LASER DIFFRACTION

Principle

Diffraction of a laser beam, in combination with the Polarization Intensity Differential of Scattered light (PIDS) of three wavelengths, can be used to determine grain-size distributions in the range of 0.04 to 2000 µm (Coulter LS230 Grain Sizer). For samples with particles larger than 5 microns, the Fraunhofer diffraction model is used for calculation. This model only requires refractive indexes for the medium (water) and an imaginary absorption value. For measurement of clayey samples, absorption parameters at wavelengths 450, 600, 750, and 900 nm should be known for a correct optical model.

Results of laser diffraction measurements are in volume percentages of fractions. If the bulk density of the particles in the various size ranges is similar, the volume fractions equal mass fractions.

Sample size and homogeneity

Laser diffraction requires small sample sizes. This implies that bulk samples have to be homogenized carefully before taking subsamples. For dry samples this can be done by sample splitter; for moist samples, careful mixing with a normal kitchen machine gives good results. Required sample sizes vary from about 0.5 gram for clayey samples to more than 5 grams for sands.
Because the maximum grain-size that the instrument can measure is 2000 µm, samples should be sieved to remove coarser fractions. Our experience is that coarser fractions may also damage the system's lenses. The weight of the coarse fraction and that of the fraction < 2000 µm can be determined separately.

The correct size of the sample can only be measured in the machine. Measurements are carried out either at 10% obscuration (of the 750 nm laser beam) or at 50% obscuration of the polarized light beams (50% PIDS obscuration). If the concentration of the suspension is too high, the sample can be diluted in the sample vessel. This is carried out as follows:

-       Run the circulation pump at maximum speed (this is normally also done for measurement);
-       Open the out-valve and let part of the suspension flow away (or remove part of the suspension by other means);
-       Add water to the vessel until the correct obscuration is obtained.

Our experience is that this dilution does not affect grain size distributions of samples smaller than 800 µm. Coarser samples may suffer loss of coarsest fractions.
If suspension density is too low or too high, incorrect results will be obtained.

Sample preparation

Sample preparation for laser grain sizing is similar to that for the pipette method (see Section D). The small subsamples are treated with peroxide to remove organic matter, and sonicated. Some samples may be treated with HCl to remove $CaCO_3$, or with sodium dithionite to remove free iron and manganese. The pretreated sample is transferred quantitatively to the Coulter measuring vessel, after which it can be diluted if necessary.

If samples have to be stored before analysis, they should preferably be stored in closed vessels. Ultrasonic treatment is advised before transferring the sample to the measuring vessel.

Optical models

All optical models should contain the refractive index of the medium (1.33 for pure water) and of the sample. For soil samples, a main refractive index of 1.56 is adequate, because quartz, feldspars, and clay, have refractive indexes in the same range. For samples that have a significantly different mineralogical composition, a different refractive index should be used.

Absorption parameters for the wavelengths 450, 600, 750, and 900 nm can only be obtained by direct measurement. The most convenient way is to build an optical model for populations of samples with more or less the same properties. Absorption of the suspensions can be measured by removing part of the suspension from the sample vessel after diffraction measurement at the correct obscuration. The absorption properties of this suspension - which should not be allowed to settle - can be determined directly by photospectrometer. Means of absorption properties of a number of similar samples should be used to obtain the optical model for such samples.

Colour of the sample has a stronger effect on its optical properties than mineralogy. Therefore, it may be necessary to build different optical models for, e.g., brown and red samples, or for untreated and deferrated samples.

For Dutch soils on river sediments, we obtained the following absorption parameters (peroxide treated clayey samples, no removal of iron):

wavelength	absorption 10% obscuration	absorption 50% PIDS
450 nm	0.13-0.35	0.04-0.12
600 nm	0.10-0.22	0.04-0.09
750 nm	0.09-0.17	0.03-0.06
900 nm	0.05-0.12	0.02-0.05

The absorption scale runs from 0 (no absorption) to 1 (100% absorption).

Flocculation

Because in the grain sizer, the sample is mixed with tap water, there is a real risk of flocculation. Flocculation in clayey samples usually appears in the range around 400 μm. Flocculation may be reduced by sonication, but is not always fully removed. Addition of dispersant (sodium hexametaphosphate or sodium pyrophosphate) is advised. The dispersant does not significantly alter the refractive index of the medium.

Air bubbles

If very cold tap water is used in the system, air bubbles may form, which appear as a specific grain size fraction in the measurement (60-200 μm). Air bubbles disappear upon sonication. If the problem is serious, the instrument should be connected to a large storage tank, and not directly to the tap. In the storage tank, the water warms up and loses the dissolved air.

Correlation with sieving and pipette analysis

For sandy samples, there is a very good agreement between the results of sieve analysis and laser diffraction, although slight shifts in median may be found. For determination of clay percentage, correlations between pipette analysis and laser diffraction have to be established for each population of samples. Although correlations tend to be good, they are never 1:1. This implies that also clay/silt/sand percentages by laser diffraction will deviate from those by pipette analysis and sieving.

Remarks

-        Once measured, results can be recalculated with different optical models.

-        At normal measuring times (90-120 seconds) and measurement at 2 obscurations, some 20-40 samples can be measured per day. Rinsing and calibration take considerable time.

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Section G

USE OF SOIL ANALYSES AND DERIVED PROPERTIES

by P. Buurman

Introduction

As mentioned in Section A, soil analyses are usually carried out on the 'fine earth' fraction, which is the fraction smaller than 2 millimeter. This fraction is obtained by sieving the samples over an adequate sieve. Information on the relative amount of fractions coarser and finer than 2 mm should be given in any soil analysis, but this is frequently omitted. Nevertheless, this information is extremely important for, e.g., land evaluation and quantification of soil genetic processes.

Some researchers tend to regard soil analytical data as an absolute truth that can be extrapolated to, e.g., a mapping unit. Similarly, boundaries between units in soil classification systems are sometimes rigidly defined, both with respect to properties that are measured directly and to properties that are calculated from direct measurements. It is clear that such unwavering belief in the outcome of soil analyses will lead to serious misrepresentations.

The results of soil analyses carried out by a first class laboratory, are accurate and reproducible to within a 5-10% error, but the same analysis carried out by different laboratories will frequently give a different accuracy, even if the reproducibility is similar. Properties that are calculated from the primary analyses - and most chemical criteria in soil classification are such *derived properties* necessarily have a larger error than the primary measurements.

The problem of extrapolation is a crucial one. The lateral chemical variation of properties within a soil profile that seems to be homogeneous, can be very large indeed. Although few detailed studies exist of the short-distance lateral variation of chemical properties (e.g. Brown, 1979), such studies indicate that, in order to characterize the soil chemically with a 90% probability, some analyses would have to be carried out on tens, or even hundreds of subsamples of each horizon. There is obviously no way around these problems, because the amount of analytical work necessary to characterize a specific soil with 90% probability, would be forbidding. It is clear, however, that we have to keep the above remarks in mind when we interpret analyses or classify soils.

Most soil analyses are carried out on air-dry, or artificially dried, material. In some cases, however, drying changes soil properties to such an extent that wet or field-moist samples should be used, e.g., in the determination of pyrite and potential acidity of water-logged soils, and in soils with appreciable amounts of allophane.
In general, samples from soils that are permanently water-saturated should be analysed without drying. Allophane tends to form strong aggregates upon drying, and textures and other properties (e.g. CEC) of such soils should be determined without previous drying.

Some soil analyses are directly used to interpret soil properties; others are recalculated to obtain parameters that are used in soil interpretation and classification. Both are discussed in this chapter. If soil names are used, these are from USDA Soil Taxonomy versions. Much of this text is from Buurman (1990).

In the following text, '1500-kPa water' is used instead of the former expressions '15-bar water' or 'water content at pF 4.2'.

1. Ash content (peat)
Ash content is used to characterize peat. It is not an official classification criterion. Peats with higher ash contents are expected to be more fertile than those with low ash contents.

2. Bulk Density
Bulk density ($g.cm^{-3}$; $kg.m^{-3}$) is usually measured on oven-dry soil. In most soils, the volume of the soil does not shrink appreciably upon drying. Allophane-rich soils, however, shrink considerably. Therefore the bulk density of such soils is based on the volume of the soil at field capacity (pF 2.5; 1/3 bar; 33 kPa) and the weight of the oven-dry soil.
The bulk density at field moisture capacity is used in the classification of soils with andic properties. The present boundaries are: <0.90 for andic properties, 1.0 for andic subgroups. A histic epipedon consisting of sphagnum peat should have a BD of <0.1 $g.cm^{-3}$.
Vertisols as well shrink considerably upon drying, and bulk density could be defined in a similar way. It is, however, not a classification criterion in these soils.

3. Carbonate
'Carbonate' usually means carbonates of calcium, such as calcite and aragonite. Carbonate determinations are less accurate when samples have very high contents, such as may occur in soil horizons with calcite accumulation or in limestone rocks, or very low contents.
The standard method, which uses cold reaction, does not fully dissolve dolomite ($CaMg(CO_3)_2$) and probably only part of siderite ($FeCO_3$). Because soil pH is buffered around 8 by the presence of carbonate, pH values below 7 indicate that free carbonates are not present in amounts that can be determined by the standard methods.

Uses ***a. Calcium carbonate equivalent***

a. Calcium carbonate equivalent
The calcium carbonate equivalent disregards the presence of carbonates other than $CaCO_3$. All measured carbonate is attributed to this single phase.

4. COLE (Coefficient of Linear Extension)
The Coefficient of Linear Extension is defined as the ratio of the difference between moist length and dry length of a clod, to its dry length (L_m-L_d)/L_d. L_m is the length at 33 kPa tension (field moist) and L_d is the length when dry. This coefficient is used to define vertic subgroups. The criteria vary with the moisture regime of the soil: >0.05 in Xeric regimes, >0.07 in Ustic regimes, and >0.09 in Udic regimes.

5. Cation Exchange Capacity and exchangeable bases
The determination of exchangeable bases is fairly straightforward. The most common interference is that of dissolution of soluble salts in saline, calcareous and gypsiferous soils. In such soils, the sum of exchangeable bases is usually higher than the CEC.

CEC-NH₄OAc (ammonium acetate pH7). Because CEC of many soils is strongly pH-dependent, CEC determination offers a number of serious problems. The standard CEC determination with ammonium acetate is based on percolation of a 'fine earth' sample at a fixed pH (pH=7). Contact between percolating solution and soil sample is not optimal in such a determination. This may result in a CEC that is related to field circumstances because also in the field contact between plant roots or soil solution and solid phase is not optimal. On the other hand, the set pH of 7 results in an overestimate of the actual CEC in acid soils; while it is an underestimate for the CEC under optimal contact.

CEC-Bascomb. Contact between solution and solid phase is better in the $MgSO_4$-$BaCl_2$ method, but this method cannot be used for soils with an appreciable fraction of allophane. Allophane may preferentially adsorb sulphate - and Mg through the adsorbed sulphate, so that the measured CEC is much lower than that in ammonium acetate. The $MgSO_4$-CEC is determined without pH buffering, and the obtained value is a measure for field CEC at values close to the pH-KCl (or $CaCl_2$) of the soil.

CEC by Sum of Cations. For some soils, especially the calcium carbonate-saturated ones, CEC is determined at pH8. This is effected by the Barium Chloride-Triethanolamine method (Ba-TEA), where titratable acidity to pH 8.2 is added to the exchangeable bases. This method is used because in soils in which the pH is buffered around 8 by the $CaCO_3$ equilibrium, the CEC at pH 7 is an underestimate (dissociation of organic matter increases with increasing pH and in sesquioxides the surface charge is neutral to slightly negative above their point of zero charge).

Ammonium retention or CEC in unbuffered NH₄Cl
Ammonium retention in an unbuffered extract was formerly used instead of the ECEC that is discussed below.

Uses: **a. CEC at pH7 (CEC7)**
b. CEC at pH7 of the clay fraction (CEC7/clay)
c. CEC by sum of cations (CECS)
d. CEC by sum of cations of the clay fraction (CECS/clay)
e. Unbuffered CEC or ammonium retention/clay (NH₄/clay)
f. CEC-delta value (ΔCEC)
g. Base saturation on CEC7 (BS7)
h. Base saturation on CECS (BS8)
i. Exchangeable Sodium percentage (ESP)
j. Natric ratio
k. Sodium adsorption ratio (SAR)
l. Index of accumulation (in podzols)
m. CECS/1500-kPa water
n. Sodium saturation on CECS (Na/CECS)

a. CEC-pH7 (in 1M NH₄OAc) (CEC7)

The cation adsorption capacity of the soil is usually recalculated on a clay basis. Formerly, Dystrandepts (USDA) however, needed to have a CEC of >30 cmol(+)/kg soil.

b. CEC7/clay

The CEC of the soil (CEC7), recalculated on clay fraction basis, is used in the classification of highly weathered soils. In soils with high organic matter contents, the value is bound to be too high. Kandic and Oxic horizons should have a CEC7/clay below 16 cmol(+)/kg clay; oxic and kandic subgroups have CEC7/clay below 24 cmol(+)/kg clay.

Because CEC7 determination with the NH_4OAc method uses aggregated soil, this recalculation will usually be an underestimate of the real exchange capacity of the clay fraction.

c. CECS

CECS is used for two purposes: 1) the actual CEC in soils with a pH buffered by calcium carbonate, and 2) a measure of the potential CEC of a soil. The 'potential' CEC was used to identify soils with a high amount of pH-dependent charge (see CEC-delta value, 5f).

d. CECS/clay

This is a measure of CEC at pH 8.2, related to the clay fraction. It is used to distinguish soils with high amounts of amorphous material. In soils with 'andic properties' this value should be higher than 150 cmol(+)/kg clay (disused).

e. NH₄-retention/clay (NH₄/clay)

Ammonium retention (at soil pH), recalculated on a clay basis, was used in the classification of highly weathered soils. It has been replaced by ECEC/clay, which should give a similar value.

f. CEC-delta value

The CEC-delta value is the difference in CEC between soil-pH (Ammonium retention or ECEC) and pH8.2 (CECS). A high CEC-delta value indicates large amounts of variable charge due to sesquioxides, allophane, and/or organic matter. It was used to characterize volcanic soils.

g. Base Saturation on CEC7 (BS or BS7)

Base saturation with respect to Cation Exchange Capacity at pH 7 is commonly used to identify saturated and unsaturated soils. Boundaries used in USDA classification are 35, 50, 60, and 75%, depending on climate and CEC of the soil or clay fraction.

h. Base Saturation on CECS (BS8; BS/CECS)

This base saturation is used in the subdivision of Alfisols and Inceptisols from dry regions.

i. Exchangeable sodium percentage (ESP), Sodium saturation
Exchangeable Sodium Percentage or Sodium Saturation (exchangeable Na as a percentage of CEC7) is an indication of saline soils. It is more than 15% in the natric horizon and in natric and sodic subgroups.

j. Natric ratio (Mg+Na)/(Ca+Extractable Acidity)
This ratio is used for the identification of natric great groups, in which it should exceed 1. A high ratio usually leads to low structure stability, and transport of clay, silt, and organic matter through the profile.

k. Sodium absorption ratio (SAR)
The SAR is used to compare the composition of irrigation water with the expected ionic composition of the adsorption complex of soils treated with such water. It is defined as $(Na^+)/\sqrt{[(Ca^{2+})^2+(Mg^{2+})^2]}$. The SAR is used to identify Natric horizons and natric/sodic subgroups. In these horizons/subgroups it SAR should be higher than 13.

l. Index of Accumulation (Acc.Ind)
This index is a measure for the accumulation of amorphous matter (with high variable charge) and is used for the identification of the spodic (B) horizon. The index for each subhorizon is determined by subtracting half the clay percentage from the CECS and multiplying the result with the horizon thickness in cm. Values for subhorizons of the presumed spodic horizon are added up. The factor 0.5 with which the clay content is multiplied reflects a supposed CEC of the clay fraction of 50 cmol(+).kg^{-1}.

m. CECS/1500-kPa (15 bar) water
This property was used in Soil Taxonomy to separate Andic subgroups, for which this ratio should be higher than 1.5.

n. Na/CECS
The sodium saturation on CEC by Sum of Cations is/was used in Soil Taxonomy to separate Natric subgroups of Alfisols.

6. Electrical conductivity (EC, EC$_e$)

Electrical conductivity is measured both in irrigation waters (EC) and in soil extracts (EC$_e$). It reflects the presence of water-soluble salts. In irrigation waters it is a measure of the hazard to plants. The EC is expressed in dS(iemens).m^{-1} (previously: mmho or mS.cm^{-1}); 1 mS.cm^{-1} equals 10 dS.m^{-1}). Values below 20 constitute no hazard to plants. Higher values affect consecutively more crop species.
EC$_e$ is measured in two ways: in the 'saturation extract', and in the 1:5 soil:water extract. Both values can be used to judge salinity of soils.
Salic horizons have an EC $\geq$30 dS.m^{-1} in a 1:1 soil:water extract.

7. Extractable aluminium and acidity

Extractable (exchangeable) acidity is determined for two main reasons: 1) to determine the range in exchange capacity between field pH and pH=7 (from ECEC to CEC7), and 2) to determine the soil's buffer capacity if liming is required.

The extractable acidity is composed of H^+ ions and Al^{3+} ions in various states of hydration, such as $Al(OH)_2^+$ and $Al(OH)^{2+}$. Sometimes the extractable aluminium is determined separately in the same extract (KCl-extractable aluminium).

KCl-extractable aluminium is used to determine the 'Effective' Cation Exchange Capacity, or ECEC.

> *Uses:* **a. Effective CEC (ECEC)**
> **b. Aluminium saturation on ECEC (Al-sat)**
> **c. Effective CEC of the clay fraction (ECEC/clay)**
> **d. Base saturation on ECEC (BS/ECEC)**
> **e. Extractable acidity on ECEC (H/ECEC)**
> **f. Extractable aluminium**

a. ECEC (Effective CEC) or Permanent Charge (PC)

The Effective CEC of acid soils is an approximation of the CEC of the soil under field circumstances (at field pH). The ECEC is defined as the sum of exchangeable bases plus KCl-extractable aluminium. It is mainly used to characterize severely unsaturated soils. In some Oxisols, the ECEC is very low: Acric groups have an ECEC <1.5, and acric (acroxic) subgroups an ECEC of <2 cmol(+).kg clay^{-1}.

b. Aluminium saturation on ECEC (Al-sat)

Aluminium saturation is the percentage of the ECEC that consists of adsorbed aluminium. High aluminium saturations (>70%) usually have toxic effects on commercial crops.

c. Effective CEC per Clay (ECEC/clay) or Permanent Charge per Clay (PC/clay)

Because most of the Effective CEC resides in the clay fraction (not counting organic matter), it is recalculated on a clay basis. This value can be used to substitute NH_4^+ retention and is used in the identification of the Kandic and Oxic horizons. For these horizons, the ECEC/clay should be lower than 12 cmol(+)/kg clay.

d. Base Saturation on ECEC (BS/ECEC)

Base saturation on Effective CEC is the part of the ECEC that is due to exchangeable bases. BS-ECEC and Al-sat together make 100%.

e. Exchangeable Acidity/ECEC (H/ECEC)

Exchangeable H is the non-aluminium part of the acidity that is measured by titrating a 1M (less frequently: 2M) KCl extract of a soil to pH 7. It is a measure of the potential increase in CEC of the soil upon increase in pH (liming). In this case, it is expressed relative to ECEC. This ratio had to exceed 1 for andic

subgroups in early versions of Soil Taxonomy.

f. Exchangeable aluminium
Exchangeable (KCl-extractable) aluminium can be very high in acid soils. Alic subgroups should have more than 2 cmol(+).kg^{-1} of Al. Some acid volcanic soils may have as much as 15 cmol(+).kg^{-1}.

8. Fibre content (peat)
Fibre content is defined as the part of organic matter that is coarser than 0.15 mm. It is used to characterize the decomposition in peat soils. Peats with fibre contents of more than 75% are fibric, with 16 to 75% fibres they are hemic, and with less than 16% fibres, they are sapric.

9. Gypsum
Gypsum is a common accumulation in soils of (semi)arid regions. Although gypsum is not toxic to plants, its fairly high solubility may upset the cation balance for plant nutrition. In addition, cementation by gypsum may cause impenetrable layers. The determination of gypsum should be carried out after the removal of sulphate salts that are more soluble. In soil samples that have large amounts of gypsum, the amount of weighed soil may have to be reduced. Gypsum crusts or gypsum-cemented parts should be powdered before extraction.

10. Iron and aluminium
Iron and aluminium are mobile in acid soils, and relatively immobile in tropical soils at neutral pH. In addition, iron is very mobile in reduced form. Both metals are found in organic complexes, poorly crystalline and crystalline (hydr)oxides, and poorly crystalline silicates. In addition, both are important for stabilization of soil structure. Exchangeable or dissolved Fe^{2+} and Al^{3+} may occur in amounts that are toxic to plants. Various kinds of iron and aluminium compounds are commonly determined: Total 'Free' Fe/Al, 'Amorphous' Al/Fe, and 'Organically-bound' Al/Fe. In addition, exchangeable aluminium can be determined (see 7).

'Free' iron and aluminium. 'Free' iron and aluminium is a term for non-silicate bound Fe and Al, extracted by dithionite-citrate (with or without additional bicarbonate; DCB). With the dithionite extraction method, virtually all non-silicate iron is extracted, except for well-crystalline iron minerals such as magnetite (and some hematite). Because the method is based on reduction (Fe^{3+} -> Fe^{2+}), it is less specific for aluminium. Therefore, we prefer not to determine aluminium in DCB. In addition to Fe, also Mn can be determined in DCB. We do not usually determine Si in the dithionite extract.
For iron, DCB is supposed to extract 1) the organically-bound fraction (Fe^{2+} forms less stable complexes than Fe^{3+}), 2) the amorphous or low-crystalline iron, and 3) the crystalline iron phases. A view of iron dynamics in soils is obtained by comparing 'crystalline', 'amorphous', and 'organic' forms.

'Amorphous' iron, aluminium, and silica. The term 'amorphous' encompasses all forms which are not well-crystalline, including metals in organic complexes and in allophane. In practice, the 'amorphous' components are determined by buffered acid extraction in oxalate-oxalic acid.

In soils which contain allophane and imogolite (volcanic soils and soils on other rocks rich in weatherable minerals), the oxalate extraction extracts an appreciable amount of the amorphous components. By removing aluminium and iron from the silicate structure, also SiO_2 is dissolved. Therefore, in volcanic soils, Al, Fe, and Si are determined together in the oxalate extract.

Because oxalate dissolves most of the organic-metal complexes, it is also used as a measure of the sum of 'amorphous' and 'organically bound' Fe and Al in acid soils, such as podzols and volcanic soils. In soils with high amounts of organically-complexed Fe and Al, however, pyrophosphate may be a more effective extractant than oxalate.

The oxalate extraction is performed on dried fine earth, without further grinding. In volcanic soils, use of aggregates may result in an underestimate of the actual fraction of amorphous silicates, because part of this fraction cannot be reached by the extractant. Soils are not ground before extraction, because grinding increases the amount of amorphous components, also if crystalline minerals are ground. Oxalate may also extract (part of) the volcanic glass.

In soils that have high amounts of allophane, a higher extract:soil ratio should be used or the extraction should be repeated. End-over-end shaking is more effective than reciprocal shaking.

'Organic' aluminium and iron. Many soils, especially podzols and andosols, may contain appreciable amounts of metals in organic complexes. The organically-bound metals are extracted at high pH (the pyrophosphate extract has a pH of 10) to minimize the dissolution of other iron and aluminium compounds.

In most soils it is sufficient to determine Fe and Al in this extract, but some soils may have appreciable amounts of other organically-bound elements, such as Mn.

Because pyrophosphate is a non-organic reagent, it is possible to determine dissolved carbon in the extract. Carbon in the pyrophosphate extract is commonly used as a measure of the organic matter that is bound to metals. Carbon to metal ratios give an idea of the saturation (and the acidity) of the organic complexes.

Iron (II) and Iron (III). This is not a common determination in soil samples. Iron (II) is usually determined when mineral formulae are required or when a soil analysis is recalculated to a mineralogical composition. The analysis may be useful for soils which have pyrite, and thus potential acidity, but in this case the determination could be replaced by a sulphur determination.

Uses: **a. Total 'free' iron**
b. total 'amorphous' iron (ferrihydrite)
c. pyrophosphate to dithionite (Al+Fe) ratio
d. pyrophosphate (Fe+Al) to clay ratio
e. pyrophosphate (Al+C) to clay ratio

f. pyrophosphate-Al to oxalate-Al ratio
g. free iron to total carbon ratio
h. calculated allophane content
i. allophane in clay
j. aluminium to silica ratio in allophane
k. oxalate extractable Al + 1/2 Fe
l. colour of pyrophosphate extract
m. optical density of oxalate extract (ODOA)
n. melanic index
o. oxidic soil mineralogy

a. total 'free' iron (Fe$_d$)
Total free iron is sometimes used as a relative measure of weathering in Oxisols (accumulation of weathering products) and of accumulation in podzol-B horizons. Furthermore, it is used for comparison with extracted amounts of 'amorphous' and 'organically-bound' iron. Petroferric material normally has a Fe$_2$O$_3$ content of $\geq$ 30% (Fe$_2$O$_3$ = 1.43 * Fe$_d$).

b. total amorphous iron (Fe$_o$)
Total amorphous iron, sometimes corrected for the organically-bound iron (Fe$_p$) is used to calculate (free) ferrihydrite contents in soils (%ferrihydrite = %Fe$_o$ * 1.7). Some poorly drained podzols have very low amounts of Fe$_o$ because of lateral removal of reduced iron (<0.1% in Alaquods).

c. pyrophosphate Fe+Al to dithionite Fe+Al ratio (Al$_p$+Fe$_p$)/(Al$_d$+Fe$_d$)
The ratio of pyrophosphate-extractable to dithionite-extractable iron and aluminium is used in the identification of the spodic horizon (podzols, spodosols). (Al$_p$+Fe$_p$) stands for the organic matter-bound metals; (Al$_d$+Fe$_d$) for the 'free' aluminium and iron. By definition, the spodic horizon should be dominated by organically-bound Al and Fe, and therefore it should have a ratio of >0.5.

d. pyrophosphate Fe+Al to clay ratio (Al$_p$+Fe$_p$)/clay
The ratio of pyrophosphate-extractable Al+Fe to clay is used in the identification of the spodic (B) horizon, mainly to separate it from clayey and allophanic soils. It relates the amount of organically-bound sesquioxides to the mineral colloidal fraction of the soil. In the spodic horizon, the ratio should be larger than 0.2.

e. pyrophosphate Al+C to clay ratio (Al$_p$ + C$_p$)/clay
In soils with very low iron contents, this criterion replaces the former in the identification of the Spodic (B) horizon. In the spodic horizon, the ratio is higher than 0.2.

f. pyrophosphate Al to oxalate-Al ratio (Al$_p$/Al$_o$)
In soils that contain both allophane and organically-bound Al, this ratio is used

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to determine the relative importance of both. Pyrophosphate-extractable Al stands for organically bound Al, Oxalate-extractable Al for the total 'active' Al fraction.

g. free iron to total carbon ratio Fe_d/C

This ratio is used for the identification of Ferrods, Humods and Ferric Podzols. In Ferrods and Ferric Podzols, the ratio should be 6 or more; in Humods the ratio should be less than 0.2

h. Allophane in soil

Allophane in soil is calculated from oxalate-extractable Si, by multiplying with a constant. The method supposes a fixed percentage of Si (14%) in allophane or a variable Al/Si ratio which depends on the oxalate-extractable Al, according to: % allophane = $100 * Si_o / \{23.4 - 5.1 * (Al_o-Al_p) / Si_o\}$.

The former calculation is based on a fixed formula for allophane ($Al_2O_3.SiO_2.$ 2.1 H_2O), while the latter uses a variable allophane composition in order to allocate all extracted Al and Si to allophane. This may lead to errors in soils that contain allophane and either or both of gibbsite and (plant) opal.

i. Allophane in clay

Because most of the allophane is found in the clay fraction, the calculated allophane is sometimes recalculated to the clay fraction. This value is an approximation of the amount of allophane in the clay. Because allophane, however, is not restricted to the clay fraction, the estimate is not very useful.

j. Al/Si in allophane/imogolite

This ratio indicates the composition of the 'allophane' fraction in the soil. The ratio is calculated by subtracting the organically bound Al from the total 'active' Al, and dividing the result by oxalate-extractable Si (see also 10h).

k. oxalate-extractable Al + 1/2 Fe (Al_o + 0.5Fe_o)

This is a criterion of oxalate-extractable matter for Andisols and Spodosols. It is used because in Andisols both amorphous aluminium and amorphous iron are a measure of soil development. It is calculated by adding half the amount of oxalate-extractable Fe to the amount of oxalate-extractable Al. Other criteria for Andisols depend on this value, which should be more than 2.0 in soils without volcanic glass and >0.25 in soils with 30% of volcanic glass. The value should be >1% for andic subgroups of Oxisols. Spodic subgroups have a value of ≥0.25.

l. Colour of pyrophosphate extract (peat)

The colour of the pyrophosphate extract of peat samples is used to determine the amount of sapric (fully decomposed) organic matter. For dominance of sapric material, the colour value and chroma should be darker than 5/1, 6/2, and 7/3.

m. Optical density of oxalate extract (ODOA)

High optical density of the oxalate extract ($\geq$ 0.25) is used to characterize spodic materials.

n. Melanic index

Many andosols have a thick, dark-coloured humus horizon. This horizon has properties which are very different from those of other surface horizons. Typical andosol dark surface horizons are called 'melanic epipedon'. The melanic epipedon is characterized by a 'melanic index', which is a colour index of the 1:100 soil:0.5M-NaOH extract. The melanic index (MI) is defined as: absorbance at 450 nm / absorbance at 520 nm. The melanic epipedon should have a MI of $\leq$1.65

o. Oxidic soil mineralogy

Soils have an oxidic mineralogy when iron oxides constitute a substantial part of the soil, when compared to clay minerals. Soils are oxidic when iron-oxide and gibbsite constitute more than 20% of the clay percentage: $(1.43^*Fe_d + 2.88^*Al_d)$/clay $\geq$ 0.2.

11. Moisture content

The determination of moisture content in the context of chemical analyses is only for the expression of measured properties with reference to oven-dry soil. If water-retention properties of the soil are required, these should be measured at specific moisture tensions (see Water retention).

12. Nitrogen

Nitrogen is determined in two basically different ways: 1) after combustion of the sample; 2) after wet oxidation (Kjeldahl)

N determination after combustion is carried out with a C/N analyzer. It is a measure of the Total Nitrogen in the sample. In the Kjeldahl method, organic matter is digested with sulphuric acid, after which ammonium is measured in solution. Because the Kjeldahl method does not determine the nitrate fraction, values determined by this method are lower than total N. Nitrogen is the important element in organic matter dynamics. Therefore, it is used as an indication of soil fertility. Nitrogen occurs in the soil as part of organic molecules and as inorganic NH_4^+, NO_3^-, which can be determined separately, and minor amounts of NO_2^-. Mineralization converts organic into inorganic N. Nitrification converts ammonium into nitrate, and denitrification (anaerobic) does the opposite. In addition, organic matter decomposition may result in the production and emission of nitrous oxides.

Ammonium. Ammonium ions in the soil are in equilibrium with NH_3 in the gas phase. At high pH, NH_4^+ is easily converted to NH_3, so that ammonium may be lost during the determination, both from samples and standards. It is therefore good practice to acidify the solutions in which ammonium should be measured.

Uses: ***a. C/N ratio***
       b. N mineralization

a. C/N ratio
This ratio is an indirect indication of the fertility status of the soil. High values indicate incomplete mineralization of organic matter and/or low nutrient status. In agricultural soils and in most tropical soils the value is around 10. In litter, the C/N ratio may be 30-50.

b. N mineralization
Nitrogen mineralization is measured when the dynamics of the organic matter is studied. Inorganic nitrogen (NH_{4+} and NO_3^-) are measured before and after a specific period of incubation of the sample at a specific temperature. N mineralization rate is a measure of the natural availability of nitrogen for a non-nitrogen fixing vegetation.

13. Organic carbon
There are two essentially different ways of determining the organic fraction in soils.
1) direct measurement of carbon
2) measurement of oxidizeable material.
The direct measurement of carbon is carried out through complete combustion of the sample and measuring the evolved CO_2. In soils with considerable amounts of charcoal (burnt grasslands, burnt forests) this leads to an apparent C content that is much higher than the 'organic matter' or 'humus' fraction of the soil. To convert measured carbon to 'humus', usually a conversion factor of 2 is used (humus has about 50% of organic carbon; the other 50% consists of oxygen, hydrogen, nitrogen, and sulphur).

The calculation of soil organic matter through measurement of oxidizeable material (methods of Walkley-Black and Kurmies), is based on the supposition that the level of oxidation of organic substances in the soil is constant. This is certainly an over-simplification, although it may be true for similar soils under similar circumstances. It is certainly not true when, e.g., well-drained and hydromorphic soils are compared. The wet oxidation method has the advantage that charcoal is not oxidized. On the other hand, the conversion factor from oxidizable material (milli-equivalents oxidant used) to weight of organic matter (usually 1.72), is highly empirical. The presence of manganese interferes with the method.

Uses: ***a. Organic C content in topsoils***
       b. Organic C in kg/m^{-3}

a. Organic C content in topsoils
An organic C content of 0.7% (1% OM) is a requirement for mollic and umbric horizons (USDA). Humods have >6% organic C in part of the spodic horizon.

b. Organic C in kg.m⁻³

b. Organic C in kg.m^{-3}

Organic matter in kg.m^{-3} is used in the classification of highly weathered soils, because in such soils, the cation exchange capacity is dominated by organic matter rather than by clay minerals. The value is calculated by adding up the contents of all horizons to a depth of one metre. For each horizon, down to a depth of one metre, the organic carbon content (%) is multiplied with the bulk density (kg.dm^{-3}) and with the thickness of the horizon in dm. Boundaries are >12 for Humic great groups of Alfisols, Inceptisols and Ultisols, and >16 for Humic subgroups in Oxisols.

14. Oxide molar ratios

Molar ratios of total oxide contents of soils or clay fractions (SiO_2, Al_2O_3, Fe_2O_3) are used to evaluate relative accumulation and loss of these compounds in horizons of, a.o., Oxisols. In these soils, silica tends to be more mobile than aluminium, while the movement of aluminium and iron depends on pH and reduction/oxidation processes.

> *Uses:* **a. Al_2O_3/Fe_2O_3 molar ratio**
> **b. SiO_2/Al_2O_3 molar ratio**
> **c. SiO_2/Fe_2O_3 molar ratio**
> **d. SiO_2/R_2O_3 molar ratio**

a. Al_2O_3/Fe_2O_3 molar ratio

This molar ratio is used to - on a profile basis - compare the relative movement of Al and Fe as a result of soil formation.

b. SiO_2/Al_2O_3 molar ratio

This molar ratio is used to - on a profile basis - compare the relative depletion of Si versus Al, as a result of soil formation.

c. SiO_2/Fe_2O_3 molar ratio

This molar ratio is used to - on a profile basis - compare the relative depletion of Si versus Fe, as a result of soil formation.

d. SiO_2/R_2O_3 molar ratio

This molar ratio is used to - on a profile basis - compare the relative movement of Si versus sesquioxides, as a result of soil formation

15. Particle-size analysis

Classical particle-size analysis is based on a combination of sieving for the fractions 50(32)-2000μm and sedimentation for the finer fractions. Many laboratories do not use sieves finer than 50 μm. Sieving is a fairly accurate method, especially if the grains are rounded. The sedimentation method is prone to inaccuracies. Firstly, the coarse silt fraction in suspension settles too fast, so that errors may occur when coarse silt is abundant. On the other hand, if the fraction 32-50 μm is also determined by sieving, the sieving time needs to be prolonged, and the sieve fraction 32-50μm or 32-64μm

is bound to become more inaccurate.

The sedimentation method gives reproducible results, if used properly. Care should be taken that the sedimentation cylinders are never in direct sunlight. Dispersion may be a problem in some soils. Most soils disperse easily in an alkaline medium, but especially in allophanic soils this may create problems. Our experience is that many allophanic soils disperse better in an acid medium (pH 3-4), but prolonged contact with a low-pH dispersing medium will result in dissolution of allophane and, again, flocculation. Soils with strong aggregation may need sonication to improve dispersion.

Recently, we have used laser diffraction for grain-size determination. Although the results are excellent for sand and silt-sized materials, correlations vary for clay-sized material. Therefore, laser diffraction estimates of grain-size fractions for soils can only be used once correlations with the sieve/sedimentation method have been established.

Uses: *a. soil texture class*
   b. fine clay/clay ratio
   c. silt/clay ratio
   d. sand/clay ratio
   e. water-dispersible clay

a. soil texture class:
Texture classes are usually based on percentages of fractions <2, 2-50(64), and 50(64)-2000µm, which together constitute the fine-earth fraction. Texture classes are sufficiently wide to accommodate inaccuracies in grain-size determination, except in cases where a small difference in e.g. clay, would result in a different classification. The experimental error in clay and silt determination is in the order of 5% .

b. fine-clay/clay ratio
Fine clay is determined by centrifugation after dispersion of the sample. The result of the determination depends on the applied centrifugal force (expressed as gravity, *g*). Change in centrifuge type may result in different results. For correct determination, the rotation speed leading to the correct *g* should be determined for each centrifuge.

The fine-clay/clay ratio is used to indicate clay illuviation in soils: illuvial horizons have higher fine-clay/clay ratios (and higher CEC_{clay}) than overlying and underlying horizons. Because both the determination of clay and that of fine clay are prone to large errors, the ratios have no absolute value, but can be used to compare related samples that were analyzed in the same batches. The ratio is not used in soil classification.

c. sand/clay ratio
The sand to clay ratio is used to characterize weathering in soils of arid regions (Aridisols).

d. silt/clay ratio
The silt to clay ratio is used to characterize weathering in ferralitic soils (Oxisols). Because weathering in such soils tends to result in dissolution of the silt fraction and formation of clay, highly weathered soils have low ratios (<0.2).

e. water-dispersible clay
Many tropical soils, especially Oxisols, have very strong aggregation. Without pretreatment, the soils do not disperse in water. The clay content that is measured by just shaking the soil with water, compared to the clay content after pretreatment, is an indication of strength of aggregation.

16. pH
It is common practice to determine the pH of a soil both in water and in an electrolyte solution (1M KCl or 0.01M $CaCl_2$). pH in 0.01M $CaCl_2$ is closest to field circumstances in the soil. The soil:solution ratio influences the concentration (and activity) of the hydrogen ions, and therefore, pH determination is always carried out at a fixed ratio, usually 1 gram of soil : 5 ml of water. In acidic soils, the addition of an electrolyte causes additional dissociation of H^+ from negative surfaces and leads thus to a lower value of the measured pH. In soils with appreciable amounts of positively charged surfaces, OH^- may be set free by the addition of electrolyte solution, thus leading to an increase in pH. pH is measured in the clear supernatant, because measuring in suspension (proximity of charged surfaces with adsorbed H^+) may give a lower reading, especially in water.

> Uses: **a. pH-H_2O**
>   **b. pH-KCl/$CaCl_2$**
>   **c. pH-NaF**
>   **d. pH-H_2O_2**
>   **e. delta-pH**

a. pH in water
pH in water is used to characterize peat soils and for the identification of the sulfuric horizon. Sulfuric horizons should have a pH (1:1 water:soil) of ≤3.5. Spodic materials (USDA 1994) should have a pH (1:1, water) of ≤5.9. Sulfidic materials should have a drop in pH of at least 0.5 unit when incubated under aerobic circumstances at room temperature.

b. pH in KCl (or $CaCl_2$)
pH in KCl is a criterion used for the distinction of Acric groups in Oxisols (pH in 1 M KCl should be 5 or higher). pH in 0.01M $CaCl_2$ is used for characterization of soil fertility. Acid soils have a pH (2:1 liquid:solid, 0.01M $CaCl_2$) of less than 5.0; Nonacid soils a pH >5.0.

c. pH-NaF
The pH-NaF is used to identify soils with a high amount of exchangeable OH^-

groups, such as andosols. Soils with allophane have high amounts of exchangeable OH^-. The addition of a NaF solution results in exchange of F^- for OH^-. The OH^- is set free in the solution, resulting in an increase in pH. Most andosols have pH-NaF above 9.5, and frequently around 10.5.

Also other soils with large sesquioxide surfaces, such as iron-rich oxisols and B_{hs} horizons of podzols, may have a high pH in NaF.

d. pH-H_2O_2

pH in hydrogen peroxide is used to estimate acid sulphate soil potential. The hydrogen peroxide rapidly oxidizes pyrite and induces a drop in pH if pyrite is present.

e. delta-pH

Delta-pH is the difference between pH-KCl and pH-H_2O. If the value is negative, the soil has a dominance of negatively charged surfaces (normal situation in humus and clay-dominated soils). If the delta-pH is positive, the soil has a dominance of positively charged surfaces. This may occur in iron-rich or gibbsite-rich ferralitic soils (Anionic subgroups), in andosols, and in podzol-Bs horizons.

17. Phosphorus

Phosphorus is an essential element for plant growth. It strongly influences root development. Phosphorus determinations comprise 'total' and 'available' phosphorus. Total phosphorus is an acid extraction which should also extract phosphate from minerals such as apatite. It is a measure of the phosphate-reserve in the soil. For short-term agricultural practice, however, use is made of so-called 'available' phosphorus. Phosphorus available for plant growth is determined by less aggressive extractions, of which the Bray (I or II) and Olsen extractions are examples. The Olsen extraction is used for alkaline soils, while the Bray extraction is used in acid soils.

> *Uses:* **a. Phosphorus retention**
> **b. P_2O_5 in 1% citric acid**

a. phosphorus retention

Some soils have a high capacity to immobilize phosphorus (phosphorus fixation). This is of prime importance for agriculture, because phosphorus added to such soils is easily converted into non-available fractions. This effect is especially strong in andosols, which have high amounts of active aluminium. Therefore, phosphorus retention from an acidified solution of preset P concentration, is used to recognize andosols (>85% retention within 16 hours contact).

b. P_2O_5 in citric acid

Soils that have received long-term fertilization by stable manure have high phosphate contents. To separate such man-made horizons from mollic surface

horizons, they should have more than 1% of P_2O_5 dissolvable in 1% citric acid.

18. Soluble salts

Water-soluble salts strongly determine the osmotic pressure of water and thereby the availability of water to plants. Water-soluble salts, in practice, are those salts which are more soluble than gypsum. They comprise simple compounds, such as NaCl (halite), but also complex salts with more than one kind of cation and/or anion.

Water-soluble salts are common in 1) soils of (semi) arid regions, where weathering products are not leached, and 2) soils that have been inundated by sea water. Soils with appreciable amounts of water-soluble salts usually have pH of 8 or higher, and a high electrical conductivity (EC_e, see there).

In soils with water soluble salts, measured base saturation is always higher than 100% and therefore the determination of BS does not make much sense. On the other hand, if base saturations above 100% are encountered, and the dominant cation is not Ca^{2+}, soluble slats are usually present.

19. Sulphur

We have included two sets of procedure to determine suphur fractions in the soil. The first set is meant for soils in general, the second is specific for (potential) acid sulphate soils.

The first set of determinations contains:

- Total sulphur by complete oxidation and subsequent reduction of all sulphur compounds.
- Inorganic, esterbound, elementary, and part of sulphide sulphur, by strong reduction (hydriodic acid)
- Organically bound sulphur by mild reduction (nickel).

The second set of procedures includes a more detailed fractionation of inorganic sulphur fractions. It contains:

- Total sulphur by complete oxidation to sulphate
- Elementary sulphur by extraction with acetone
- Soluble sulphates, including gypsum, by Na_3EDTA extraction
- Jarosite (Jarosite ($KFe_3(SO_4)_2(OH)_6$ is an oxidation product of pyrite, which forms in acid soils. It has a pale yellow colour and can remain stable over a long period. The amount of jarosite is a measure of oxidized pyrite (FeS_2) in acid sulphate soils).
- Pyrite (Pyrite (FeS_2) is a sulphide which is common in sediments that have accumulated in coastal, vegetated zones, such as mangroves or reed marshes. Upon aeration of the sediment (e.g. artificial drainage), pyrite oxidizes to sulphuric acid, which may considerably decrease the pH of the soil. Pyrite is determined to assess the potential hazard of acidification upon oxidation).

Water-soluble sulphur

Water soluble sulphur is used in the identification of the sulfuric horizon, which should have more than 0.05% Instead of EDTA, water is used for extraction.

20. Water retention
Water retention at specific suctions is used to calculate water that is available to plant growth, and hydration of the fine-grained soil phases such as clay, allophane, and organic matter.

Commonly used suction (pF) values are: 0 (water-saturated soil), 2, 2.3, or 2.5 (field moist), and 4.2 (permanent wilting point for plants). pF values are the negative logarithm of the matric suction expressed in cm water pressure. pF 4.2 = 15 bar = 1500 kPa. At low matric suctions, water is bound in aggregation pores; at suctions above pF 4.2, water is only bound to mineral surfaces.

Uses: ***a. available water***
> ***b. water content at 1500 kPa (pF 4.2, 15-bar)***
> ***c. clay, calculated as 2.5 * (water at 1500 kPa - % organic carbon)***
> ***d. n-value***
> ***e. total pore volume***
> ***f. rapid drainage pores***
> ***g. slow drainage pores***
> ***h. clay to 1500kPa-water ratio***

a. available water
Available water is water, in a soil without saturated flow, that is available to the plant. It is expressed as the difference in water content between 1500 kPa and field capacity. It is an important criterion in suitability classification of soils.

b. water content at 1500 kPa
The water content at 1500 kPa represents the water that is bound on clay surfaces and not in the pore system. It is used to separate subgroups in Andisols (USDA): Hydric subgroups have water contents at 1500 kPa of more than 70% by volume, while Vitric suborders and subgroups have water contents at 1500 kPa that are lower than 15% (air-dry samples).

*c. Clay calculated as 2.5 * (% 1500kPa-water - % organic carbon)* ; formerly 2.5 or 3 * 1500kPa-water
If soils have high contents of free iron and/or aluminium it may be very difficult to obtain full dispersion for clay determination, and the pipette method may give values that are too low. Therefore, an estimate of the clay fraction is used, e.g., in the classification of Oxisols. If the calculated clay fraction is higher than the fraction determined by pipette analysis, the calculated clay fraction ($\leq$100 %) is used in calculation of CEC-clay.

d. n-Value
The n-value, or ripening factor, is a measure of the amount of water bound by mineral and organic matter (in field conditions). It is used to classify soils with respect to their capacity to withstand deformation and to bearing capacity. The expression of the n-value is by the formula: $n = (A - 0.2R)/(L + 3H)$, in which A is the water content of the soil in field condition (%); R is the non-clay fraction

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of the fine-earth (%); L is the clay content (%), and H is the organic matter content. Soils that are not fully ripened have an n-value of more than 0.7 (e.g., Hydraquents).

e. total pore volume
Total pore volume is calculated by subtracting the dry bulk density of a ring sample from the bulk density upon saturation, and multiplying the result by 100.

f. rapid drainage pores
The volume percentage of rapid drainage pores is calculated by subtracting the water content at pF 2.0 from the water content at pF 0.

g. slow drainage pores
The volume of slow drainage pores is calculated by subtracting the water content at pF 2.5 from the water content at pF 2.0.

h. clay/1500kPa-water
This ratio, or its reverse, is used in Soil Taxonomy for the separation of Andic Subgroups. The reverse ratio (1500kPa-water/clay) is also used to describe (not define) the Oxic Horizon. Andic subgroups have a ratio of 1500kPa-water/clay of less than 1.25.

Water analyses
Water analyses are carried out both on water percolating through the soil, which is obtained through suction cups, on rain water, throughfall, stemflow, and on surface and ground water.
The purposes of water analyses can be: 1) to obtain an impression of water quality, 2) to obtain insight in water movement through the soil or the landscape, 3) to measure changes in composition as water moves through the soil (solid-liquid interaction; which elements are retained, which are set free), 4) to obtain an impression on stability of soil minerals.

Water analyses may comprise 1) major elements, salts; 2) trace elements; 3) organic compounds.
Major elements are measured to measure e.g. transport/residues of fertilizer application (N, P, K). In natural areas, the measurement may be used to calculate weathering rates or landscape budgets. Some major elements, such as Al and S are analysed to study acidification due to atmospheric pollution. Trace elements are mainly analysed to measure pollution.
Organic carbon levels in natural waters are influenced by agrochemicals, but they also vary in natural systems. Especially in acid (acidified) systems, organic carbon levels in natural waters (dissolved organic carbon, DOC) can be high: waters of podzols, fens, peats.

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