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Agricultural Chemistry

Part X of

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X.

AGRICULTURAL CHEMISTRY

by

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The following are the chief institutions in Holland, engaged on agricultural-chemical research: the Agricultural Chemical Laboratory of the Agricultural University (Landbouw-Hoogeschool), Wageningen; the Agricultural Experimental Station and Soil-Science Institute T.N.O., Groningen; the Laboratory for Soil Research (Bedrijfslaboratorium voor Grondonderzoek), Groningen; the Laboratory of the Soil-Science Section of the Wieringermeer Administration (North-East Polder Works), [Laboratorium van de Bodemkundige Afdeeling der Wieringermeerdirectie (Noordoostpolderwerken)], Kampen; the Chemical Section of the Central Institute for Agricultural Research, Wageningen; the State Agricultural Experimental Station, Maastricht (especially for the testing of fertilisers). The laboratories attached to the Experimental Gardens at Naaldwijk (Zuidhollandsch Glasdistrict), Aalsmeer and Boskoop, carry out investigations specially directed towards horticultural problems, more particularly towards vegetable growing, floriculture and culture of ornamental trees, respectively, while the Laboratory for Flower Bulb Research (Bloembollenonderzoek) at Lisse carries out similar work for bulb-culture.

Agricultural-chemical research consists chiefly in the chemical examination of soils, crops and fertilisers. In the following, investigations on each of these topics are discussed separately under the appropriate headings.

Soil research.

Chemical examination of soils may take place in connection with manuring and fertility problems. Such investigations are carried out in particular, at the Agricultural Experimental Station and Soil-Science Institute, institutions concerned principally with researches on the fertility of the soil and the way crops are affected by it.

For characterising the fertility of the soil it is important to have a knowledge of the entire available sources of the various plant nutrients. In this connection there is a tendency not to restrict the examination to surface samples but to discover the composition and

the properties of deeper layers in order to obtain a more complete picture of the nutritive medium of the crops, the pedosphere.

The methods of investigation, used for this purpose, must be so arranged, therefore, as to allow of these sources being discovered. For manuring recommendations for example, one does not determine the total content of a food constituent but the amount available for the plant.

For this purpose it is important to determine accurately the correlation of the figures obtained by various methods of examination with the yields from test plots. The method, which gives the best correlation, gives the best picture of the condition of the food component in question and therefore forms the best basis for the advice.

In the section under "analytical methods", published and unpublished researches on this topic carried out during the years of the war, are collected and discussed.

Chemical investigation of the soil may also be carried out in order to characterise different types of soil as a part of soil surveys over smaller or larger areas. For characterising soil-types it is necessary to study the structure of the soil-profile and to examine chemically the layers, which can be differentiated in it. Thus chemical examination of a podsol profile, consisting of the following layers, mull, ash-grey sand, black layer, brown sand and yellow sand, gave a clear picture of the differences in the contents of iron, aluminium, silica, and non-exchangeable magnesium in these layers, from which, amongst other things, could be definitely deduced the occurrence of leaching of sesquioxides from the grey-sand layer (A_2 -layer) and flocculation in the darker coloured B-layer below it, in connection with which reference may be made to refs. (1) and (2).

An experiment is described in ref. (3), in which river sand was covered with heath mull; percolating resulted in the artificial formation of a grey-sand layer.

Which crop can best be grown, depends in many cases on the structure of the soil profile, so that examination of the profile structure is necessary from this point of view also.

The connection between profile structure and the crop is clearly brought out in ref. (4).

Soil-profile surveys in any particular area are of importance for judging the agricultural value of the soils in question. Data may be obtained in this way for schemes for land-reclamation, re-allocation projects and concerning the suitability of the soil for a particular type of cropping, e.g. horticulture, the laying down to orchard, etc.

This belongs already to the domain of soil mapping. Ref. (5), (6) and (7) deal with such investigations in which chemical examination was linked up with field surveying.

A similar investigation has been carried out in the north-west region of the province of Friesland in the municipalities of Het Bildt, Barradeel and Franekeradeel. The results, so far obtained, have been published in a couple of cyclostyled reports. From these investigations it appears that the clay-humus substance in the top soil in Het Bildt has greater base-combining powers than that in the top soil from the Dollard polders, which contain a few per cent more of calcium carbonate than the first mentioned soils, but are a few hundred years younger. This greater base-combining power of the clay-humus substance shows itself mainly in the fact that it holds rather more lime and rather more magnesia in adsorbed state.

In the above mentioned investigations, physico-chemical examination, mechanical examination being emphasised particularly, is also necessary. In this connection reference may be made to ref. (8), in which the characteristic distribution and summation curves for various types of soil are given in connection with the formative or selective agent (especially flowing water or wind). For classifying the whole region a number of main types were developed mainly for sandy, loam and loess soils (see Physico-chemical researches).

Chemical examination of the surface soil and of the various soil layers affords an insight into changes, undergone by the various soil components as a result of the ageing of the soil and of the effects of climate, cultivation, and cropping practices. Examination of these changes is of importance for knowing the condition of fertility of the soil and the measures necessary to bring the soil into a suitable state of fertility.

A satisfactory soil condition requires a certain content of humus in the soils. It is pointed out in ref. (9) that it is of great importance that this humus be stable, *i.e.* that it does not lose the property of binding and releasing water and that it is resistant to biological influences. The soil is maintained for long periods in a crumbly condition by this stable humus. The authors in question claim to have succeeded in preparing such a humus-substance and give the method of preparation. They also describe experiments they have carried out with this artificially produced humus.

A stable humus product is being produced on a larger scale by the N.V. Calha at Zwijndrecht. At the request of the Director of Agricultural Research experiments are being carried out with this

Calha-humus on 60 experimental plots on sea-clay and river clay. The supervision of these field tests rests with the Government Agricultural Advisers.

In connection with the humus question mention should also be made of ref. (10) in which it is discussed whether the humus content of the soil can be increased by supplying stable manure and green manuring. From field trials it does appear that stable manure sometimes increases the humus content of the soil. This increase does not continue, however; with continued organic manuring humus content remains constant at a somewhat higher level.

According to an unpublished paper by the same author, liming has no appreciable effect on the humus content of most soils with the exception of peaty clay soils.

Mention may also be made of the following communications.

In ref. (11) there is described the mode of formation and the mechanical composition of the clay and loam soils in the Province of Groningen, together with their contents of organic matter, nitrogen, sulphur, phosphoric acid and potassium.

As regards the organic matter it is emphasised that the content in the various types of soil is constant and independent of the method of manuring.

The fixation of nitrogen from the atmosphere is dwelt upon in great detail.

According to ref. (12) some sandy soils appear to have a mineral potash reserve of some significance, from which potash is easily made available as in sea-clay soil, as distinct from potash-rich river-clay soil, which gives up its potash with difficulty.

Ref. (13) deals with the loss of lime from the cultivated layer of humus-sandy soils the first year after liming. On 16 experimental plots the average loss in lime a year after liming was 30 % (extreme cases about 50 %) and the average amount of lime not combined with humus 40 % (extreme cases 70 %).

The effects of basic slags and of carbonate of lime in the p_H and the V-value for an acid sandy soil rich in humus are compared in ref. (14). On account of the adsorptive fixation of large amounts of phosphoric acid in the humus-complex, it is possible for the humus to fix more lime. This lime causes the V-value to rise relatively more than the p_H of the soil when compared with the same amount of lime fixed from calcium carbonate.

Lysimeter tests are particularly suitable for obtaining a picture of which parts of the soil components are washed out by the rain, are

taken up by the crops and are retained in the soil under conditions of normal cultivation and manuring. From a complete chemical examination of rain water, drainage water, harvested crops and manures it is possible to make up a balance for the various soil components. The results of such an investigation are given in ref. (15).

In the examination of soils for horticultural purposes one has frequently to contend with other problems than those met with in agriculture, because, as a rule, one is dealing with a special crop on a special soil. In ref. (16) reasons are stated why, in the examination of the peaty clay soil at Boskoop, attention must be paid to the composition of the soil, the degree of acidity and the nutrients in connection with the requirements of the various plants (bushes, pyramids, etc.). When earthing up the garden ground, as is necessary at regular intervals in the culture of ball plants, the humus content can be increased, if desired for some particular crop, by making use of peaty earth, excavated from peaty polders, which possesses a high humus content (50—80 %). Mud (25—60 % humus) is less suitable in this case.

Another problem in horticulture requiring a great deal of attention is the over-salting of the soil, which can occur under glass, particularly in greenhouses. This over-salting may be the result of watering the plants with brackish water, but also from the high fertiliser dressings, which are used in horticulture. Since percolation with rain water is eliminated in greenhouses, the excess of salts cannot be taken away by the water draining through the soil. The salt content of the soil may become so high on this account as to damage the plants. Hence the determination of the salt content of greenhouse soil is very necessary. Ref. (17), (18), (19) and (20) deal with this over-salting.

From all investigations it appears that the highest salt content occurs in the upper layer particularly in a surface layer of 2 to 3 cm. It is recommended therefore to remove the uppermost layer of greenhouse soil every year and replace it with fresh soil from outside.

Practical observations indicate that the critical salt-limit lies at 300—400 ppm chlorine in the soil solution. Experiments to establish this limit are described in ref. (21).

Finally, mention must be made of researches arising from flooding with salt water as a result of war conditions. These researches deal with the detrimental effect, which these inundations have had on the structure of the soil as a result of the more or less

complete replacement of exchangeable lime by exchangeable sodium. They consist chiefly of determinations of the sodium chloride content of the soil water and of the exchangeable sodium content of the adsorption complex (see "Analytical Methods").

Investigation of the decrease in the sodium chloride content of the soil water is necessary to determine when the ground can be reseeded successfully. The sodium must be removed from the complex and replaced by calcium. This can occur in three ways: by hydrolysis; by exchange with calcium bicarbonate produced by the interaction of carbon dioxide and calcium carbonate in the soil; and by replacement with lime from a dressing of gypsum; [see ref. (22)].

Similar examinations as described above have also been carried out in connection with the North East Polder soils. Details of this investigation can be found in ref. (23).

Crop research.

Chemical examination of crops as such certainly belongs to agricultural chemistry. However when the figures obtained in this investigation are used to obtain an insight into conditions of plant growth by correlating the contents of various components with various conditions of the soil, as is done at the Agricultural Experimental Station and Soil-Science Institute T.N.O., chemical examination of crops can be included without objection in biochemistry. The researches of Dr. E. G. Mulder, in which a chemical examination of the crop serves to elucidate in what manner certain food-elements influence the nitrogen metabolism of the plant, lie mostly in the domain of applied bio-chemistry.

• For a summary of investigations carried out on this subject during the war years reference may be made to the epitome on "The significance of biochemistry on research at the Government Agricultural Experimental Station and Soil-Science Institute".

Researches on the chemical examination of crops, which lie in the domain of techniques, are discussed in the section on "Analytical Methods".

Researches on fertilisers.

The passing of the Fertilisers Order (Meststoffenbesluit) in 1942, marks an important advance for consumers and bona fide dealers of fertilisers.

Dealing is allowed only for substances named in a *List of*

fertilisers attached to the order, and for which general and for the most substances also particular, requirements are laid down (this List is properly speaking an extension of the non-official Codex Meststoffen, in force previously) and further, for such goods as the Director-General of Agriculture shall grant exemption from the general prohibition of trading. An explanation of this Order is given in ref. (24).

The routine examination of fertilisers for content and fineness is carried out by the Government Agricultural Experimental Station at Maastricht, while work on their agricultural significance is the task of the Agricultural Experimental Station and Soil-Science Institute T.N.O. at Groningen.

In connection with the occurrence of various deficiency diseases (e.g. magnesium, manganese, copper and boron deficiency), in recent years more and more attention has been paid to the composition of the natural and artificial manures, especially as regards the secondary constituents and the content of minor-elements.

A study has been made in connection with potash manures to find out how the composition of the salts used in Dutch agriculture has varied in the course of time. The use of potassic manures of increasing grade was clearly linked up with a decreasing magnesium content in the manure employed, which makes the sandy soils, naturally poor in magnesia, liable to show, symptoms of Hooghalen disease to an increasing extent, as described in ref. (25).

In the last few years pot experiments have been used on a fairly large scale to study the effect of various lime and magnesia fertilisers on an acid, peaty, sandy soil and on a de-calcified clay-soil, especially as regards the degree and the rate of action depending on the way the lime is combined (hydroxide, carbonate, silicate) and the fineness of the products. The results will be published shortly.

On account of the scarcity of copper sulphate finely powdered copper slag has been used almost exclusively for copper dressings during the war. A number of comparative experiments have been carried out in which much attention has been directed to the take up of copper and lead by the crop (copper slags invariably contain a definite quantity of lead, an appreciable absorption of which is dangerous for both animals and man, as well as about 1 % copper and various other components). Data on this experiment are published in ref. (26).

Further, in recent years a considerable amount of research has been carried out on the composition and the manural value of

various types of town-refuse. The original town-waste in untreated form, consisting of domestic rubbish and dung, is doomed to disappear. Household and street refuse from the towns is available for agriculture in the composted state on a large scale (e.g. as V.A.M. compost. V.A.M. compost is the fermented town-refuse of the Hague). Attention has also been given to the dung components from sewage water purified in one way or another (usually as rotted sludge in Europe, and in the future, possibly by the improved activated sludge method used in America). It had already been known for a long time, that the copper deficiency on soils suffering from reclamation disease could be cured by the copper present in household refuse compost. Now, the manurial value of other components of various kinds of compost is being more closely examined. Ref. (27) contains data on the minor-elements, copper, manganese, boron and lead, present in V.A.M.-compost and town-compost.

In connection with the determination of the value of compost as a manure, a method has been worked out for estimating the coal from house-heating in compost, the determination depending on the resistance of this coal to the action of various chemicals, which remove the other components of the compost.

Analytical methods.

From what has gone before it follows that analytical methods, especially those used for soil research, depend on the aims in view. It becomes necessary therefore to choose the method, which is most suitable for the purpose in question. For this reason, it is obvious that the procedures usually employed are very conventional — the results being comparable only when obtained under rigidly prescribed conditions. Hence, it is very desirable that the analytical procedures for soil examination followed in the various laboratories should agree as far as possible. This became particularly urgent when it was decided in 1940 to decentralise soil examination in horticulture. A joint committee, composed of representatives from the Laboratory for Soil Research at Groningen and the laboratories at Naaldwijk, Aalsmeer and Boskoop, was installed for promoting unification in soil research. A technical sub-committee meets regularly and has already carried out a large amount of work on the subjects of techniques and unification.

A description of the methods employed at the Laboratory for Soil Research at Groningen is to be found in ref. (28) and ref. (29) may also be mentioned.

In the examination of soil it is also important that sampling is uniform so that comparable results may be obtained as set out in ref. (30).

In looking for the most suitable method, the accuracy required is usually the determining factor. In ref. (31) it is pointed out that in connection with his investigations, the agriculturalist needs at least three types of methods, namely, one which is only slightly inaccurate (error 1%), one with a moderate accuracy (error 5—10%) and one which may be only approximate (error ~ 30%). The more accurate the method, usually, the lower is the speed of working and the higher the cost. The various methods employed in these three types are discussed.

The classical chemical methods may be considered as the most accurate. In most cases titrimetric methods are to be preferred to gravimetric methods, since they are most quickly carried out.

Colorimetric, nephelometric, sedimentary, polarographic and spectro-analytical methods belong to those of moderate accuracy. Ref. (32) discusses the latter type of determination using flame spectra. From this discussion it appears that with Na, K and Ca ions the error amounts to about 10%, but with Mg⁺⁺ an error of about 25% must be reckoned with, the method being less accurate for this ion.

In the same class is included microbiological methods in which the effect of the element to be determined on the growth of moulds or bacteria is examined.

Owing to the shortage of glass-ware and chemicals brought about by wartime conditions, it was desirable to have alongside the chemical method, a rapid and sufficiently reliable method for determining the needs of the soil for certain constituents, e.g. potash and phosphoric acid. According to the researches described in ref. (33) the *Aspergillus* method comes into consideration for this purpose.

For determining magnesium in soil with the aid of the mould *Aspergillus niger*, according to the method of Mulder and Smith, a somewhat modified recipe has been worked out, which makes it of use for soil examination.

The Morgan-Venema method may be mentioned as an approximate method of only limited accuracy. A description of this micro-method, which depends on the comparison of colour and turbidity reactions, is given in ref. (34). The method is very rapid, at least four times as quick as the ordinary chemical analysis. The abundance of the various food constituents in the soil as determined

by this method, is not expressed as a number but in groups such as high, moderate, low, etc. This method also appears to be sufficiently reliable for a preliminary examination of soil for practical ends such as the valuation of the soil, according to ref. (35).

From tests of this procedure on various types of soil it is clear that some of these nephelometric and colorimetric analytical methods present some difficulties and call for considerable experience.

Examination for phosphate.

For determining the phosphoric acid content of samples of crops and the total phosphoric acid content of soil, a closer study has been made of the "metol" method according to the recipe of Scheel¹⁾. It rests on the principle that phosphomolybdic acid is reduced in acid solution by certain reducing agents, in this case mono-methyl-*p*-aminophenol sulphate (metol), to a blue coloured compound. Amongst other things, a study was made of the stability of the blue coloured solutions and the effect of various factors and substances, which may have a deleterious action on the blue colour. The results obtained with the "metol" method agreed well with those obtained by the gravimetric method of von Lorenz. The former method, however, is much quicker than the latter. A paper on this subject, from the Agricultural Experimental Station and Soil-Science Institute T.N.O., by Dr. J. Th. L. B. Ramaeu and J. ten Have, is in course of preparation.

The P-number is determined by allowing 5 g of soil to stand for 24 hours at 50° with 50 cm³ distilled water. Care must be taken that the temperature does not fluctuate too far from the prescribed 50° during the extraction.

In the determination of phosphate an extraction with 1 % citric acid at room temperature is usually employed for extraction in an acid medium.

Some soil samples gave a P-number, which is higher than the P-citrate figure. This anomaly has to be sought in the first place apparently, in the difference in temperature employed in the two methods, while, at the same time, p_{H} also appears to play a certain rôle, as set out in ref. (36).

Although extraction with 1 % citric acid gives the best correlation with the reaction of the crop, extraction with a lactate-buffer mixture according to Egnér has also been examined. Shaking in a ratio of 25 g soil to 250 cm³ liquid gives the most consistent

¹⁾ Scheel, Z. anal. Chem. 105, 256 (1936).

duplicate results. The actual total phosphate content can be determined only by breaking down the soil. All acid extraction methods give lower values (extraction with aqua regia according to Lemmermann, with 12.5 % nitric acid according to Hissink, or with a mixture of nitric acid and sulphuric acids according to Fleischmann).

Examination for potash.

Since various factors for the determination of potassium by the sodium cobaltinitrite method have been given by different investigators, this method has been subjected to a detailed investigation. It was at once emphasised that the method of precipitation and the washing of the precipitate obtained, had a very marked effect on the result and therefore on the factor one uses. The ratio of K : Na in the liquid appears to be of importance in determining the composition of the precipitate. In order to obtain a precipitate of constant composition, sodium chloride is added so that sodium is always present in excess. The washing of the precipitate should always be carried out with a small amount of wash-liquor.

For determining the readily available potash, extractions with water, 0.1 *n*-hydrochloric acid and *n*-ammonium acetate are used. Conclusions to be drawn from repeated extractions of the same sample with these extraction media, with regard to the forms in which potassium occurs in the soil, are set out in ref. (37).

At the same time, an investigation has been initiated on extraction with Egnèr's mono-chloroacetic acid—calcium monochloroacetate buffer mixture. This method appears to be more complicated than the usual extraction with 0.1 *n*-hydrochloric acid. The figures for potassium found by Egnèr's method appear to be only half those found by extraction with hydrochloric acid. Further details on this point may be found in ref. (38).

Ref. (39) contains a summary of the points found to be of general and lasting importance in the method of carrying out the determination of potassium.

A study has been made of the method of determining potassium devised by Schachtschabel (extraction with a mixture of ammonium oxalate and acetate). Extracts free from calcium are obtained in this way, which is a great advantage when one is using a flame photometer, since the potash in the extract can then be determined directly without further manipulation. If one is not in the possession of a flame-photometer, this method is no quicker or simpler than the others.

From the contents of potash soluble in 0.1 *n*-hydrochloric acid in soil samples from various clay regions, it appears that the potash content depends on the clay content (particles smaller than 16 μ). Various clay formations are recognisable by this relationship as pointed out in ref. (40).

Sea clay from the Province Zeeland is richest, river clay the poorest in potash. Young clay soil begins to lose potash in considerable amounts after the calcium carbonate has been washed out.

In order to obtain a clearer picture on the forms in which potash occurs in the soil, and the quantities of each of these forms, an investigation has been initiated into the content of exchangeable potash, of potash soluble in hydrochloric acid of various strengths and of the total potash contents of soil samples from various clay regions. A communication on this point from the Agricultural Experimental Station and Soil-Science Institute T.N.O., by Dr. J a c. v a n d e r S p e k is being written.

Suffice it to mention here that of the total potash content, part occurs in the clay fraction (particles with a diameter smaller than 16 microns) and part in the sand fraction and that in the lightest clay soils even more than half the total potash is present in the sand fraction.

Examination as regards the fixation of phosphate and potash.

Of a given quantity of phosphate and potash fertiliser a portion is fixed in a form not directly available for the crop. Phosphate fixation is dependent on the moisture content of the soil and whether this content remains constant or not. With regard to the fixation of potash reference may be made to item (41).

An explanation is given in this dissertation about the underlying causes of fixation of potash in a non-exchangeable form. On the basis of experiments with soils, showing different responses to manuring with potash in actual practice, it could be established that all soils containing an inorganic colloid fraction, are able to fix potash in a non-exchangeable form; potash-rich soils less and potash-poor more. On the contrary, humus soils without clay fractions fix no potassium. A picture of the form of the fixing soil complex has been made. Mica particles surrounded by a hydrolysis-humus film are considered to be the main components of the fixation complex in the soil. The power of fixation is decreased by disturbing this loosely attached hydrolysis-humus film.

Examination for:

Exchangeable bases. In soils which have been under salt water, the salts in the soil cause some difficulty in the determination of exchangeable bases. Ref. (42) indicates how these bases can be determined in this particular case. The salt content of the soil water is determined by pressing out the soil, somewhat moistened if necessary and analysing the press-liquid. From the total water content of the sample, by subtracting the so-called salt-free zone, the content of dissolved cations in the soil can be calculated. This content is subtracted from that obtained by leaching the soil with sodium chloride or ammonium nitrate. The difference forms the exchangeable bases. The occurrence of calcium carbonate and solid calcium sulphate in the soil makes it necessary to make special determinations and calculations with regard to exchangeable calcium.

Magnesium. Small amounts of magnesium cannot be determined by the hydroxyquinoline method of Berg²⁾ according to the original prescription. A larger excess of hydroxyquinoline and ammonia is necessary. This brings about a lowering of Berg's theoretical factor.

In the determination of the exchangeable magnesium in the soil by extraction with 0.1 *n*-hydrochloric acid it is possible to remove the interfering humus compounds with a very pure nitrite preparation. The separation of silica can then be ignored.

In the extraction of acid soils (p_{H} below 5.5—6.0) with 0.1 *n*-hydrochloric acid or with 1 *n*-ammonium chloride, for the determination of magnesium, the removal of sesquioxides in the solution can be ignored if sufficient ammonia and ammonium chloride is added before the extraction, to prevent the solution of Fe, Al or Mn and phosphates.

Sodium. A comprehensive investigation has been carried out on the determination of sodium by the magnesium uranyl acetate method. The ratio in which Na and K occur in the soil extract is very important by this method. The investigation has shown that inaccurate results can be obtained by the occlusion of potassium in the uranyl acetate precipitate. This can be prevented by a correct choice of the ratio solution : reagent, which is dependent in its turn on the ratio Na : K and also on the absolute quantities of these components.

²⁾ R. Berg, „Die analytische Verwendung von *o*-Oxychinolin (Oxin) und seinen Derivaten“, Stuttgart 1938, Ferdinand Enke Verlag.

Sesquioxides. Iron and aluminium can be determined in the presence of one another in the same sample of soil extract by Berg's hydroxyquinoline method. This method gives more reliable figures, especially for aluminium, than the indirect method (subtraction of the Fe_2O_3 -content from the sum of precipitated and ignited Fe_2O_3 and Al_2O_3). With hydrochloric acid extracts of soils it is necessary first of all to remove the humus compounds, e.g. by igniting the dried residue with ammonium nitrate; (cf. ref. (43)).

Very divergent results were obtained, as stated in ref. (44), in the determination of the iron content of a series of samples with 0.1 *n*-hydrochloric and 1% citric acids at ordinary room temperatures and at temperatures in centrally heated rooms.

The determination of sesquioxides is of importance, e.g. in studying the displacement of iron and aluminium in soil profiles and in investigations on the phenomenon of phosphate fixation by the soil. For this purpose the contents of these components are determined by means of acid extractions at different concentrations at the boil.

The total contents of Fe_2O_3 , Al_2O_3 and P_2O_5 were also determined for some humus sandy soils, separately in the humus and sand respectively, the soil being separated mechanically with carbon tetrachloride into fractions rich and poor in humus. In all the humus-sandy soils examined the Fe_2O_3 and Al_2O_3 -contents of the humus appeared to be much higher than those of the sand, while practically all the phosphate appeared to be combined with the humus complex.

Minor elements. Most attention has been paid to the determination of copper, lead and zinc, both in soils and in crops. The urgency of examination for copper and lead was increased during the war years by the use of finely ground copper slags containing a certain amount of lead as fertilisers. It is of great importance to know whether crops take up any of this feared poison.

Since the chemical method for determining copper in soil is pretty tedious, the determination is carried out with the aid of *Aspergillus niger* and so worked out that it is useful for practical soil examination as indicated in ref. (45).

An attempt has also been made to carry out the determination of copper by extracting the soil with acid followed by electrolytic separation of the metal. The method is applicable to crops but presents difficulties with soil e.g. incomplete separation due to the

presence of iron. These difficulties have now been solved to a great extent.

Since the carrying out of the above mentioned determinations offers some difficulties and different methods of working are employed by the various institutions, which vary rather in accuracy, in 1944, a working committee of the Kopercommissie T.N.O. was set up, on which expert workers of all kinds had seats. This Committee has the commission to set up a more general method for the determination of copper, lead and zinc in soil extracts, crop samples and animal material. So far it has mainly been concerned with crop samples and animal material. The Committee has not yet arrived at setting up a definite recipe. For determining copper, lead and zinc the dithizone method is being studied (zinc interferes with the determination of copper) and for copper in crop samples and animal material, the "carbamate" method (sodium diethyldithiocarbamate) according to the prescription of Nydahl³⁾. The method of Fischer and Leopold⁴⁾ is being examined more closely for the determination of zinc. A colorimetric method of determination is being sought, which will be suitable for photometric examination.

With regard to manganese, reference may be made to the paper in ref. (46). According to this investigation Richards'⁵⁾ potassium periodate method does not give good results. Too low values are found due to evaporation with sulphuric acid while ash from grass appears to occlude manganese. Replacement of sulphuric acid by phosphoric acid gives higher and more reproducible values for the manganese content of grass.

It is generally known that a disease may appear in some agricultural crops in alkaline soils due to lack of manganese. This disease can be cured by administration of manganese sulphate. This phenomenon also occurs according to ref. (47) in horticulture. According to experiments described in this paper roses usually require a p_{H} of about 6.5. Chlorosis may occur in soils with higher p_{H} -values. Strewing manganese sulphate has little effect but good results were always obtained by spraying.

Nitrogen. The use of selenium in place of mercury in the determination of nitrogen in soils allows the time of destruction to

³⁾ F. Nydahl, Z. anal. Chem. 116, 315 (1939).

⁴⁾ H. Fischer and G. Leopold, *ibid.* 107, 241 (1936) and Aluminium 25, 356 (1943).

⁵⁾ Richards, Analyst 55, 554 (1930).

be considerably shortened both in the Kjeldahl and Jodlbauer methods.

Chlorine. It is not possible to base an accurate determination of the chlorine content of natural soil samples on a measurement of the electrical conductivity. The chlorine content can be measured both accurately and quickly, however, by means of a direct determination in the soil by a potentiometric method using a Ag—AgCl electrode. Details are given in ref. (48).

Sulphate. When the sulphate is precipitated as BaSO₄, after separation of Fe, Al, PO₄, etc. with ammonia, in hydrochloric acid solutions containing significant amounts of iron and aluminium, appreciable amounts of sulphate are carried down in the separation if there is an excess of Ca-ions present in the extract as for example in soils containing carbonate. If the separation of sesquioxides is left out, as a rule good results are obtained although the precipitate may possess a brownish tint.

Physico-chemical investigations .

The following investigations of fundamental importance for agricultural research, must in our opinion be included in this summary, although they are more physical in character, nevertheless a fair proportion is based on chemical research.

A new method of determination for granulometric examination embracing all fractions has been worked out (a combined sieve and pipette method), in which all the fractions are determined directly and not one of the fractions calculated as a remainder (difference from 100 %); see ref. (49).

After pretreatment of the soil with 30 % hydrogen peroxide and 0.2 *n*-hydrochloric acid it is filtered off on a Büchner funnel and washed free from electrolytes. The soil is then passed in the wet state through a sieve with a mesh diameter of ± 35 microns. What passes through the sieve is peptised with 0.005 molar sodium oxalate and separated by means of a special pipette into seven sub-fractions. What remains on the sieve is divided into eleven sub-fractions on a shaking sieve-device.

In the North East Polder there are soils in which the 0—2 micron fraction is 60—70 % of the 0—16 micron fraction and others in which it is only 30—40 %. In a number of soils from both groups has been looked for a relationship, which exists between the contents of the 0—2 and the 0—16 micron fractions on the one hand and the

adsorption, fatness, compressibility, abrasive power, plasticity and shrinkability of the soil freed from humus on the other. The correlation of these latter quantities with the 0—2 micron fraction appears to be much closer than with the 0—16 micron fraction, in fact for most properties correlation with the 0—2 micron fraction is extraordinarily close. As a consequence, the classification of North East Polder soils, which has been based hitherto on the 0—16 micron fraction, has been altered to a classification based on the content of the 0—2 micron fraction; (cf. ref. (50)).

For methods for determining the above mentioned units reference may be made to a paper (51) which is at present in type.

Various researches relate to the water in the soil. For the permeability of the soil for water and its behaviour on drying, reference may be made to publications (52) and (53).

From ref. (52) it appears that if the soil solution contains little salt, the saturation of the adsorption-complex (varying ratio of Ca : Na) is of no significance for the speed at which the soil will lose its water when exposed to evaporation.

The saturation of the complex has a very great effect, however, on the permeability; a clay with a Ca : Na ratio of 7 : 3 and the same porosity is about 5 times less permeable than a pure Ca-clay.

The permeability depends very much on the porosity.

It is well known that, with peaty soil, if the ground water table is lowered, an irreversible drying may occur, which is very detrimental to crops. For projected water level lowering and reclamation of peaty land, it is important to know beforehand whether the chance of this irreversible drying exists. In order to determine this a method has been worked out by Hudig⁶⁾, in which a disc of the peat is dried and allowed to take up water again. The amount of water taken up and the alterations in volume are a measure of the extent of the irreversible drying to be expected.

Ref. (53) contains the results of examination carried out by this method.

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