

CONTRIBUTION TO THE STANDARDIZATION OF THE METHODS OF ANALYSIS FOR HEAVY METALS IN SEDIMENTS

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This paper deals with sampling procedure, conservation and preparation of the sample prior to analysis, chemical analyses, and finally presentation of the analytical results.

SEDIMENT SAMPLING AND CONSERVATION

SAMPLE COLLECTION

For the investigation of the most recent layer of sediments in the sea, lake or river bed, it is sufficient to take the uppermost centimetres of sediments with a grab sampler. Studies, which focus on just the uppermost skin of bottom sediments and the interactions that take place across the sediment-water interface, make very specific demands on sample recovery, as this skin must be removed relatively undisturbed. A box coring device may be sufficient to retrieve this interface, otherwise sampling by divers may be necessary. For stratigraphical studies, piston corers and gravity corers are used, particularly for sampling the deep-sea floor.

There are different principles on which most types of grab samplers work:

- a) A pair of weighted semi-cylindrical jaws press into the sediment by their own weight while they are open. When the device is lifted, the two jaws close by their own weight or by a tension spring.
- b) An open sampling box cuts into the sediment and is closed from below by a mechanism when it is raised.

The important difference between the two methods is that with the box type sediments can be taken in their original, nearly undisturbed, state. The more simple excavator type, however, is better suited for coarser sediments and is superior for that material to the sampling box types, as the complicated closing mechanism of the latter is often jammed by gravel.

Several types of grab samplers of the excavator type are used. These devices are easy to handle and have

minimal requirements for ancillary shipboard equipment. Different modifications of this type include: the Franklin-Anderson grab (121), the Dietz-La Fond grab (116; 121), the Petersen grab (121; 129), the Ponar grab (23; 49; 56; 83), the van Veen grab (40; 41; 44; 48; 51; 69; 76; 80; 81; 82; 99; 103; 129), the Smith-McIntyre grab (19; 127), and the Shipek grab (9; 20; 21; 22; 49; 112; 116; 117; 121; 123; 130; 144). The Shipek bottom sampler is somewhat different from the other grabs of the excavator type mentioned. A half-cylindrical steel bucket is lowered in an inverted position until it comes into contact with the sediment. The bucket is then forced to rotate at high speed by a pair of springs and thus it cuts in a continuous curve through the sediment completing a rotation of 180°. The body of the sampler protects the bucket from washout on ascent. On shipboard the bucket is released, yielding an undisturbed sample. Although the grabs of the excavator type are designed for sampling the upper centimetres of bottom sediments, it is also possible to collect the uppermost skins of those sediments. For that purpose the grab is opened carefully on shipboard and then the top layer of the contents is subsampled.

However, box corers are better suited for taking almost completely undisturbed samples of the top layer. Moreover, the contents of the box can be divided into different layers. Different types of box corers used are: the Birge-Ekman dredge (3; 71; 121; 136), the Reineck box corer (33; 39; 65; 92; 95; 99; 109), the Auerbach-Wippermann grab (8; 91; 92), and the Soutar-Gamble corer (42; 85). A disadvantage of subsampling different sediment layers from the box corers is the fact that this must be done by removing successive slices downwards from the top side of the

sample within the box. This disadvantage may be overcome by subsampling the box core with small plexiglass cores; a method which will result in smaller samples, however. Another possibility is the use of the Jenkin mud sampler. This sampler consists of an open perspex tube provided with lids at each end, which are closed mechanically after the tube has been thrust into the mud. By introducing a piston into the lower part of the tube, after it has been hauled up, the mud column can be lifted upward and can easily be divided into several slices. We have successfully used the Jenkin mud sampler in collecting sediment profiles to a depth of about 60 cm, as have other investigators (3; 4; 72; 84; 90).

Although most box corers and the Jenkin mud sampler are suitable for sediment profiles, piston corers are specially designed for profile sampling. These corers consist of a plastic liner which is generally screened by an outer steel barrel with a length ranging from 10 cm to 6 metres. The upper side of the liner is closed by a valve or a piston before the barrel is hauled up, which protects the core from washout. Different types of these corers are: the Benthos gravity corer (66; 117; 121), the Alpine corer (121), the Phleger corer (43; 104; 121), the Mackereth corer (66; 146), and the Barcow pipe dredge (14). Sly (121) tested the efficiency of several types of bottom sampling devices. These tests and our own experience showed that the Ponar grab, the van Veen grab, and the Shipek grab are well suited for sampling the upper 10 to 20 cm of all types of sediments, although the Ponar grab and the Shipek grab are perhaps a little heavy for small-boat operations.

As the three samplers mentioned cause little or no disturbance, they are also suitable for collecting the uppermost skin of bottom sediments. Of the box corers, the Ekman dredge and the Reineck box corer were found suitable for profile sampling in soft clays, muds, silts, and sandy silts. Both devices guarantee the recovery of undisturbed cores, which can be subdivided into different layers. The Ekman dredge, however, should be used preferably under calm water conditions, because of its light weight. The Reineck box corer, which is much heavier, requires a boat of solid construction for operation. The Jenkin mud sampler also proved to be an excellent sampler for collecting undisturbed mud profiles which can exactly be divided into several layers, including the uppermost skin. This sampler requires a boat with a mechanical winch for operation. Of the coring devices, the Benthos gravity corer, the Alpine corer, and the Phleger corer were tested by Sly (121). These three corers were found suitable for collecting cores from sea and lake beds. Each corer, however, has its limitations. The Benthos corer, although particularly suitable for stu-

dies of the sediment-water interface even under violent ship motion, was found to be unsuccessful in sandy sediments. The Alpine and the Phleger corers were able to take cores in almost all sediment types. However, the Alpine corer is less convenient under poor working conditions. The Phleger corer has been designed specially for taking short samples of up to 0.5 m and seemed to be very suitable for sampling shallow lacustrine and estuarine deposits. However, no gravity or piston corer will penetrate more than about a metre into pure sands. Some workers have had considerable success in using vibrating corers for taking samples from sandy material.

SAMPLE CONSERVATION

To limit the biological activity in the sediment, samples are usually kept in cold storage before they are transported to the laboratories. Sometimes they are frozen on shipboard, especially when profiles or cores will be subsampled at a later stage. Craig and Morton (24) investigated the possible loss of mercury from a sediment sample upon storage at -15°C for several days, as reported by Daughdrill (28a). They found no significant loss of mercury from samples stored at -20°C , -6°C or even at room temperature. This does not agree with Daughdrill's work, but a possible explanation would be that in Daughdrill's samples the mercury was present in the form of methyl mercury.

Before further treatment, sediment samples are usually dried at several temperatures: room temperature, 30°C , 40°C , 50°C , 60°C , 80°C , 100 to 110°C , and freeze dried. In a few cases, metal analyses are carried out in moist samples, especially when exchangeable metals are to be determined. The drying temperature seems to be arbitrary. Soil chemists, for instance, prefer drying at a temperature of about 40°C , but mineralogists generally freeze dry the samples. Nothing has been reported about loss of non-volatile metals during the drying processes. Mercury, however, is sometimes intentionally determined in sediments dried at a fixed temperature. Some authors (60; 128; 142) determined total mercury in undried samples, while others (68; 83; 99) use air-dried samples. A comparative investigation on both air-dried and moist samples showed no effect of air drying on the amounts of mercury found (83).

Mercury has also been determined in sediment samples dried at various temperatures: 40°C (25; 48), $< 60^{\circ}\text{C}$ (81), 60°C (26; 93), 80°C (27; 119), and 90 to 100°C (7). A significant loss of organomercury compounds was found (60) when samples of sediments dried at 60°C were compared with undried samples. Other workers (68) compared the results from oven-

dried (110°C) sediments with those from air-dried samples and found the oven-dried sediments averaged 7% lower. On the other hand, other investigators observed no loss of mercury in sediments dried at 80°C (27) or at 90 to 100°C (7). Mercury has also been determined in freeze-dried sediment samples (21; 100; 105; 130). No detectable loss of mercury following freeze drying was reported by some authors (21; 105), but one investigator (68) found that the results from freeze-dried samples were 23% lower than those from air-dried samples. Considering the contradictory findings about some loss of mercury by volatilization, Thomas (130) suggested that the mercury value determined in freeze-dried sediments may be low and represent approximately 80% of the true values. Olausson (100) preferred freeze drying to mercury analysis. If a freeze dryer is not available, the sample should be dried in an oven at as low a temperature as possible (40°C) to prevent loss of some volatile mercury compounds.

From the preceding, it is obvious that mercury should preferably be determined in sediments that have either been air dried or oven dried at 40°C. Although all drying procedures may be acceptable, for the determination of the non-volatile metals a drying temperature of about 40°C should be agreed upon. Thus, an almost invariable sample is obtained that can be stored for a long time. The common weight basis for expressing the analytical results is the oven-dry (100 to 110°C) weight.

CHEMICAL ANALYSIS

The chemical analysis of a sediment consists of the digestion procedure and the determination of the metals which have been extracted. Within the scope of this publication, however, we will restrict ourselves to the several modes of solubilization of metals. To gain insight into the total metal contents of sediments, a rigorous digestion with strong acids, or combinations of strong acids, is generally used. Furthermore, less drastic digestion procedures can be distinguished,

ranging from a moderate attack (by which that part of the metals is mobilized that could go into solution during a period of many years) to a weak attack, corresponding with the biological availability of the metals. Below, a survey is given of the several modes of digestion.

GENERAL REMARKS ON DIGESTION PROCEDURES

A good illustration of the diversity of digestion procedures is a research project on sediments from the different sea coasts of France (National Centre for Exploitation of the Oceans, Brest, personal communication). Six different types of digestion were used:

Total attack	= HF conc. + HNO ₃ conc. + HClO ₄ conc.
Strong attack	= HCl conc. + HClO ₄ conc. + H ₂ O ₂ 30%
Strong attack	= HCl conc. + HNO ₃ conc.
Strong attack	= HNO ₃ conc.
Moderate attack	= HNO ₃ 1M + NH ₃ OHCl 0.1 M
Weak attack	= H ₂ O ₂ 30% + CH ₃ CO ₂ NH ₄ 1M

It was concluded that the differences among the results of the various forms of strong attack and moderate attack were seldom significant. A similar grouping of digestion procedures as mentioned above will be given in this survey.

Total contents of heavy metals and amounts released by strong acids

The estimation of total amounts of metals in the sediments always involves the use of HF, in most cases in combination with one or more other acids or treatments. A survey of the different types of digestion in general use is given in Table 22.

Sometimes the solubilization action is preceded by ashing the sediments (15; 44); for Cd, however, volatilization of this element was found to occur. In

Table 22. Digestion methods for the estimation of total amounts of metals

Reagents	References
HF	9; 13; 16; 97; 134
HF + HNO ₃	18; 36; 54
HF + HClO ₄	5; 33; 38; 111; 126
HF + HNO ₃ + HClO ₄	2; 108; 116; 117; 123
HF + HNO ₃ + HClO ₄ + HCl	13; 35; 44
HF + aqua regia (HNO ₃ + HCl)	77
HF + H ₂ SO ₄	106
HF + H ₂ SO ₄ + K ₂ S ₂ O ₇	29; 40
HF + H ₃ BO ₃	30; 70; 81
HF + aqua regia + H ₃ BO ₃	120

other cases fusion with $K_2S_2O_7$ is carried out (29; 40). Boric acid has been added in a number of treatments to form complexes with insoluble fluorides. Especially the teflon-bomb technique should be mentioned, which has all the advantages of working in a closed system (30; 70; 81). Digestion procedures using strong acids, without HF, are widely employed. A survey of these procedures is given in Table 23.

Some authors (39) object to the use of HCl, especially in the case of Cd (formation of volatile compounds). The use of sulfuric acid, on the other hand, should be avoided when Pb and Cd are estimated (10, formation of insoluble sulfates). A similar conclusion (deviating Pb values) could be drawn from intercalibration studies by the National Centre for Exploitation of the Oceans in Brest (personal communication).

Total metal contents (HF) versus the use of strong acids

In many laboratories the use of HF is not appreciated. Although using a teflon bomb for the digestion procedure somewhat diminishes the disadvantage of the use of HF, the method remains rather laborious. Partly for this reason other methods, involving strong acids, are used in many laboratories. It is important to be informed about the differences in action of HF and of strong acids (or mixtures of such acids) on heavy metals. Useful data on this subject, however, are scarce.

Several authors (22; 63; 124; 145) compared the solubilizing action of HF and aqua regia ($HNO_3 + HCl$). Their results are rather contradictory. Others (10; 17; 134) compared the action of HF with subsequent treatments with concentrated nitric acid and

hydrochloric acid. Here again the results are not of the same tenor. In Table 24, data (2) from Lake Ontario sediment on the use of several digestion procedures are shown as compared with a total attack including HF. It is obvious from these figures that different types of leaching procedures belonging to the group "strong attack" not always dissolve equal amounts of metals.

It is clear that diversity both in sediments and in digestion procedures gives rise to different amounts of metals extracted. In this connection diversity in sediments refers to differences in the relative abundances of heavy metals in the crystal lattices of the individual minerals. Diversity in digestion procedures refers to a greater or lesser capability for destruction of metalliferous minerals in the sediment. In view of the preceding considerations, it is advisable to carry out digestion studies for heavy metals in sediments from the relevant areas under study.

Selecting an extraction method on the basis of a minimal difference from the HF-method is one of the possibilities. Another possibility is to differentiate between the extent of destruction of metalliferous minerals in sediment. Such an evaluation of an extraction method, however, implies an intensive mineralogical analysis of the sediment before and after the extraction procedure.

Moderate and weak digestion procedures for heavy metal determinations

A number of investigators have carried out sequences of extraction procedures to achieve a more or less detailed insight into the distribution of metals over the various chemical compounds and minerals

Table 23. Digestion methods with strong acids.

Reagents	References
HNO_3	10; 12; 14; 17; 58; 86; 87; 114; 134
$HNO_3 + HCl$ (aqua regia)	39; 63; 93; 110; 124; 125; 127; 128; 131; 141
$HNO_3 + HClO_4$	44; 51; 59; 82; 103; 132; 140
$HNO_3 + HClO_4 + HCl$	145
$HNO_3 + H_2SO_4 + HClO_4$	10; 114
HCl	67

Table 24. Percentages of metals leached from a Lake Ontario sediment by three different treatments, compared with HF - HNO_3 - $HClO_4$ dissolution

Reagents	Percentages of metals leached								
	Cu	Fe	Zn	Pb	Co	Mn	Ni	Cd	Cr
$HNO_3 + HClO_4$	100	81	79	70	18	17	17	15	14
Aqua regia	80	76	71	70	16	18	14	10	44
HNO_3	88	76	75	70	16	17	16	10	45

in sediments. These procedures are known as elemental partition. The several approaches to the problem can be divided into the use of five or six subsequent treatments of the sediment, the use of three extraction procedures and the use of only two leaching procedures (all methods include estimation of the total metal contents).

A well-known example of the first group is Engler's procedure (32), by which the following five classes of metals are distinguished.

- 1) Exchangeable ions, estimated by an extraction with 1N ammonium acetate.
- 2) Easily reducible fraction, carried out with a solution of 0.1N hydroxylamine hydrochloride ($\text{NH}_2\text{OH}\cdot\text{HCl}$) in 0.01N nitric acid. This extraction presumably releases those metals which are associated with hydrous oxides of manganese and those which occur as carbonates, hydroxides and sulfides.
- 3) Organic fraction, carried out with a solution of hydrogen peroxide 30% at a pH of 2.5. By this extraction the part of the metals associated with organic solids is released.
- 4) Moderately reducible fraction, estimated with a solution that contains 2% sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_4$) and 20% sodium citrate. This extractant reduces and extracts the hydrous iron oxides and associated metals that may be brought into solution, by using moderate to intensive sediment-reducing conditions.
- 5) Residual fraction. This phase contains primary minerals as well as secondary weathered minerals which are a very stable portion of the elemental constituents. Only an extremely strong acid digestion (e.g. hydrofluoric acid) will break down this phase.

Some authors (28b; 35; 50; 51; 102) added an additional step after the first extraction to separate the metals which are associated with the carbonates. Several procedures are recommended in this respect, e.g. 1M acetic acid. The less complicated procedure of three extractions (15; 18; 108) is restricted to the estimation of the acid-reducible (the same as easily reducible), the acid-oxidizable, and a residual or resistant fraction. The acid-reducible fraction is extracted by a combined acid-reducing agent of hydroxylamine-hydrochloride in acetic acid, for the acid-oxidizable fraction Engler's solution is used.

Dutch authors (113) found for their sediments a justification for the above-mentioned procedure, finding only small amounts of exchangeable ions and negligible quantities of the moderately reducible fraction according to Engler's procedure.

Lastly a group of investigators (20; 79; 140) dis-

tinguishes, besides the total contents, only one fraction of metals, which is preferably extracted with 25% acetic acid. The latter fraction is regarded as "bio-geochemically important" and is supposed to have been incorporated into the sediments at some time during their history. Except for the first step in Engler's procedure (the estimation of the exchangeable ions), the metals which are directly available to the biota do not get much attention in the literature on aquatic sediments. In general, it may be concluded that the elemental partition studies contribute to a good insight into the geochemical differences among sediments which contain heavy metals. At least in a number of areas the procedure with three extractions is sufficient in this respect. It is doubtful, however, to what extent these procedures are helpful in distinguishing between polluted and unpolluted materials or in giving a clear insight into the geochemical history of the sediments. Furthermore, an extraction with hydroxylamine-HCl in nitric or acetic acid (acid-reducible fraction) or an extraction with 25% acetic acid is not very specific and may be replaced by several other leaching solutions.

Digestion methods for mercury

Sample digestion constitutes a critical step in the quantitative determination of total mercury. Errors can arise during digestion as a result of incomplete extraction of mercury, non-quantitative conversion of organomercury into mercury (II) ions or loss of mercury vapour (60). The complete destruction of organic material by wet chemical methods is difficult, especially in view of the temperature restrictions imposed by the volatility of mercury and some of its compounds (137). When mercury is incorporated into a research program, special attention should be given to the digestion and oxidation procedures. Many acid digestion and oxidation combinations have been used. A survey of these procedures is given in Table 25.

The basis for most work has been formed by the investigations of Hatch and Ott (55). They used cold digestion with sulfuric acid and oxidized the mixture with H_2O_2 and KMnO_4 . Mercury is then reduced to the elemental state with a mixed solution of sodium chloride, hydroxylamine-sulfate and tin (II) sulfate, and aerated from solution. The mercury vapour is then passed through a quartz-absorption cell of an atomic absorption spectrophotometer, to measure its concentration.

With regard to the many variations of the technique, as summarized in Table 25, we will only make a few remarks.

Agemian et al. (1) compared three digestion methods for mercury: (a) hydrochloric-nitric acid (1:9); (b) sulfuric-nitric acid (2:1); (c) hydrofluoric acid-

Table 25. Different types of acid-digestion and oxidation methods for the determination of mercury

Acid-digestion and oxidation solution		Temperature	References
H ₂ SO ₄	H ₂ O ₂ + KMnO ₄	cold	7; 55
H ₂ SO ₄	H ₂ O ₂ + KMnO ₄	90°-100°C	5; 107
H ₂ SO ₄ + HNO ₃	K ₂ S ₂ O ₈	cold	34; 88
H ₂ SO ₄ + HNO ₃	KMnO ₄ + K ₂ S ₂ O ₈	cold	96
H ₂ SO ₄ + HNO ₃		cold	6; 83
H ₂ SO ₄ + HNO ₃	KMnO ₄ + K ₂ S ₂ O ₈	50°- 60°C	1; 21; 60; 61; 138
H ₂ SO ₄ + HNO ₃	KMnO ₄	50°- 60°C	142
H ₂ SO ₄ + HNO ₃		50°- 60°C	81
H ₂ SO ₄ + HNO ₃		90°C	26; 27
HNO ₃	KMnO ₄ + K ₂ S ₂ O ₈	50°- 60°C	60
HNO ₃		50°- 60°C	51
HNO ₃		90°C	64
HNO ₃		120°C	12
Aqua regia		60°C	53
Aqua regia	KMnO ₄	95°C	43; 100
Aqua regia	KMnO ₄ + K ₂ S ₂ O ₈	110°C	61
Aqua regia	K ₂ Cr ₂ O ₇ + K ₂ S ₂ O ₈	110°C	24
Aqua regia		110°C	31; 39; 110; 125
Aqua regia		140°C	127; 128
HNO ₃ + HCl	KMnO ₄ + K ₂ S ₂ O ₈	50°- 60°C	1
HF + aqua regia	KMnO ₄ + K ₂ S ₂ O ₈	110°C	1
HF + HNO ₃			36
HF + H ₂ SO ₄ + K ₂ S ₂ O ₇			40

aqua regia (6:1). All extracts were digested with solutions of potassium permanganate and potassium persulfate subsequent to acid leaching.

Of the extraction methods studied, the sulfuric-nitric acid and hydrochloric-nitric acid extraction methods were found to be preferable to the more rigorous hydrofluoric-aqua regia extraction method, because of their lower detection limits, better precision, and easier analytical handling and processing. Although the first two extraction methods had very similar recovery and precision, the hydrochloric-nitric acid method has the disadvantage that when hydrochloric acid is used, violent frothing of the solution with evolution of chlorine gas occurs upon addition of potassium permanganate to oxidize the organo-mercury in the sample, which makes the analysis very cumbersome. Therefore, the sulfuric-nitric acid method, as introduced by Iskandar et al. (60) and used by many others, is recommended. If the latter recommendation is followed, however, we will have to consider the remarks of Jacobs and Keeney (61), who found Iskandar's method inadequate for examination of reduced materials in which HgS is present. In these cases the sulfuric-nitric acid mixture should be replaced by aqua regia.

PRESENTATION OF ANALYTICAL RESULTS

Within a group of co-genetic sediments, large variations in the heavy metal composition of these sediments are possible. These variations may be re-

lated to the granular composition or specific surface area of the material, as well as to the contents of organic matter, quartz-free sediment or aluminium. Furthermore, the heavy metal content of sediments can be expressed in relation to baseline levels. We will now discuss these relationships between metal content and sediment composition in detail in the next paragraphs.

METAL CONTENTS AND GRANULAR COMPOSITION

Several authors mention that the heavy metal contents of sediments depend on the granular composition of the material: higher contents in the finer-grained sediments (9; 24; 44). Others (41; 77; 78) conclude that for the interpretation of heavy metal data, information on the granular composition is needed. More quantitative information is given by some authors, who explain in more detail the relationship between metal contents and granular composition (25; 26; 71; 76; 110; 133). It may be concluded from these papers that the main portions of a number of metals are incorporated in the fractions < 20 µm. In a detailed investigation on Mn (45), the larger portion of this element was found in the fraction < 35 µm.

The significance of the granular composition to the contents of heavy metals in sediments will now be discussed under three headings.

- a) The use of correlations between metal contents and grain-size compositions.

- b) Separation of a relevant grain-size fraction and analysis of this fraction for heavy metals.
- c) The use of correlations between metal contents and specific surface areas.

Correlations between metal contents and grain-size compositions

Correlations have been studied between metal contents and mainly the fractions < 63 , < 53 , < 20 , < 16 , < 6.3 and $< 2 \mu\text{m}$. For the fractions < 53 and $< 63 \mu\text{m}$, sometimes good correlations have been found (21; 22; 52; 62; 122), in other cases the relations were less pronounced (103; 127; 128). Other investigators use the fractions < 20 and $< 16 \mu\text{m}$. Linear relationships between metal contents and these fractions have generally been found for groups of co-genetic sediments in both polluted and unpolluted areas (45; 46; 47; 48; 74; 113; 114). To characterize such a group of co-genetic sediments, these linear relationships can be extrapolated to 100% of the fraction < 16 (< 20) μm . (The contents of the fractions < 16 (< 20) μm expressed as a percentage of the CaCO_3 -free mineral constituents in the oven-dry sediment.) Another possibility is to characterize the metal content of the sediment at 50% of the fraction < 16 (< 20) μm . The latter method has the advantage of being closer to the natural granular conditions. Also a higher statistical reliability is achieved in this way. Also the fractions < 2 and $< 6.3 \mu\text{m}$ have been successfully used for correlation studies between heavy metals and sediment fractions (23; 74; 89; 97; 117).

In addition to the metal contents at 50% of the fraction $< 20 \mu\text{m}$, some authors (74) used the contents at 25% of the fraction $< 2 \mu\text{m}$. The fraction $< 2 \mu\text{m}$ has the advantage that it is more commonly used internationally than the fraction < 16 or $< 20 \mu\text{m}$. The linear relationships between heavy metal contents and the fractions < 20 , < 16 , and $< 2 \mu\text{m}$, respectively, form a sound basis for standardization procedures (metal contents calculated at 100%, 50%, or even 25% of the relevant granulometric fraction). To achieve an acceptable accuracy in this respect, at least 10 samples are needed for the characterization of the area being studied. Furthermore, the 10 samples should cover a wide range of contents of the granulometric fraction in question.

Separation of a relevant grain-size fraction and analysis of this fraction for heavy metals

Another possibility is to isolate a certain granular fraction and analyse the metals within such a fraction. Wet-sieving methods have been used to separate fractions < 61 and $< 80 \mu\text{m}$ (20; 139). The French

school isolates the fraction $< 63 \mu\text{m}$. Several German investigators separate the fraction $< 2 \mu\text{m}$ by means of the Atterberg technique (11; 12; 36; 37; 39; 40; 75; 94; 125). Objections can be raised especially to the use of the $< 2 \mu\text{m}$ fraction. As has been mentioned before, the presence of heavy metals is not restricted to the fraction $< 2 \mu\text{m}$. Furthermore, complete separation of the fraction $< 2 \mu\text{m}$ is very laborious (10–25 separation steps are necessary). If only 2 or 3 separations are carried out, the finest fractions (e.g. $< 0.5 \mu\text{m}$) are present in too large quantities. Another objection to the separation of fractions is that as a consequence of the dispersion, desorption of heavy metals may occur.

Correlations between metal contents and specific surface areas

There is only limited information available in the literature on the relationships between heavy metal contents and (specific) surface areas (25; 26; 84; 98; 101). Relationships have been found between total contents of heavy metals and specific surface area. The determination of surface areas can be carried out by BET-isotherms. Our information is insufficient, however, to be able to evaluate the relation between heavy metals and surface area.

RELATIONS BETWEEN METAL CONTENTS AND CONTENTS OF ORGANIC MATTER

There are numerous examples of correlations between heavy metals and organic matter (23; 29; 40; 52; 62; 68; 74; 75; 84; 117; 130; 131). In a number of cases special attention is focussed on the relation between Hg and organic matter. In many cases, correlations for certain metals with organic matter have been found and not for others (73; 82; 106). In some cases no correlations existed at all (25; 59). Only a few investigators use the relationship between metals and organic matter for the interpretation of their experimental results. The non-conservative behaviour of the organic matter is the cause of the lack of uniform correlations between organic materials and metals. We conclude therefore that the use of organic matter for comparison of heavy metal burdens of different sedimentation areas should not be considered.

CORRELATIONS BETWEEN METAL CONTENTS AND QUARTZ-FREE SEDIMENT

Quartz is the dominant mineral in the coarse grain-size fractions. Also, feldspar and calcium carbonate contribute to these fractions. As a consequence of their small specific surface areas, these components do not absorb mercury or other heavy metals, and can be regarded as diluters for these metals. There-

fore a negative correlation exists between the content of quartz and that of heavy metals. It is questionable to what extent the "quartz-method" can be used for the characterization of the heavy metal status of sediments instead of a linear relationship between heavy metals and a fine-grained fraction.

An alternative method should meet the following requirements.

- a) A good correlation should exist between the metal content and the relevant parameter.
- b) The regression line which indicates the relation mentioned under a) should follow the Equation $y = ax$, instead of $y = ax + b$. The function $y = ax$ implies that fewer samples need to be examined than in the case of $y = ax + b$.
- c) It should be possible to determine the parameter in a small amount of the material in question.

The Delft Hydraulics Laboratory has tested the quartz-method (115) and concluded that very good relationships exist between metal contents and the F factor ($F = 100 - (\text{quartz} + \text{feldspar} + \text{calcium-carbonate})$). Furthermore, the analysis of the F factor can be carried out in a small amount of material. Unfortunately, however, the linear relationship between metals and F factor does not follow the Equation $y = ax$ and therefore this method has no advantages over the use of the relations between metal contents and grain-size fractions.

THE PRESENTATION OF HEAVY METAL CONTENTS RELATIVE TO THE CONTENTS OF ALUMINIUM

Several authors (15; 57; 67) used the metal/aluminium ratios as a standardization procedure in heavy metal research. The greater part of the Al originates in the clay minerals, which means that the metal contents are related again to the contents of fine-grained material. At this moment, the Delft Hydraulics Laboratory and the Institute for Soil Fertility (Haren, Groningen) are carrying out investigations on the relation between Al contents and contents of the fraction $< 16 \mu\text{m}$. From these studies, it could be concluded for Rhine sediments that the contents of Al, calculated for 50% of the fraction $< 16 \mu\text{m}$, are rather constant with time. Therefore, aluminium offers good perspectives for the interpretation of heavy metal contents in sediments. Furthermore, the Al contents can be determined in small amounts of material and even in the same extracts as those for the heavy metal determinations. A disadvantage of the use of Al is, that the contents of this element in the sediments are not directly related to the hydrodynamic conditions of their environment. Additional

research is needed, however, to establish to what extent variations exist on the ratio aluminium/fraction $< 16 \mu\text{m}$ in several fluvial and marine sedimentation areas.

HEAVY METAL CONTENTS RELATIVE TO BASELINE LEVELS

The heavy metal status of sediments can also be characterized relative to baseline levels. The baseline levels of Turekian and Wedepohl (135; 143) can be used. These workers issued geochemical standard values for most metals on the basis of the mean composition of a number of rocks from different origins and ages. The advantage of these standard values is, that they are free from anthropogenic admixtures; a disadvantage is, however, that regional geochemical characteristics are not taken into account. This disadvantage can be overcome by setting up regional baseline levels. As such, more deeply located sediments can be used (37; 118), or recently deposited sediments from outside the contamination area (37). It must be emphasized that the use of baseline levels is appropriate only if the granular composition of both the material under study and the baseline sediments is the same.

CONCLUSIONS WITH REGARD TO THE PRESENTATION OF ANALYTICAL DATA ON HEAVY METALS

From the preceding paragraphs it is obvious that the linear relations between heavy metal contents and the contents of the granular fractions < 20 , < 16 or $< 2 \mu\text{m}$ form the most suitable basis for standardization of the presentation of heavy metal data of sediments. Although there is considerable experience with the fractions < 16 and $< 20 \mu\text{m}$, the internationally accepted fraction $< 2 \mu\text{m}$ may be preferred in this respect. The metal contents might then be standardized at 25% of the fraction $< 2 \mu\text{m}$. There are deposits, however, which contain only small amounts of the fraction $< 2 \mu\text{m}$, e.g. from the North Sea bottom. It is not always possible to reliably determine the metal content of these sediments at 25% of the fraction $< 2 \mu\text{m}$. Therefore, it seems desirable to use different methods for the standardization procedures for fine-grained and coarse sediments. For coarse sediments the fraction $< 63 \mu\text{m}$ should be taken into account. More information is then needed, however, on the relation between heavy metals and this fraction. Of other methods for standardization procedures, only the heavy metal/aluminium ratio seems to have possibilities. Difficulties may arise with the coarser sediments, however, in which the Al is predominantly present in the feldspar. These minerals occur in the granular fractions $< 50 \mu\text{m}$.

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