



**REGIONAL
SEAS**

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***Manual for the
geochemical analyses
of marine sediments and
suspended particulate matter***

Reference Methods For Marine Pollution Studies No. 63

UNEP 1995

NOTE:

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PREFACE

The Regional Seas Programme was initiated by UNEP in 1974. Since then the Governing Council of UNEP has repeatedly endorsed a regional approach to the control of marine pollution and the management of marine and coastal resources and has requested the development of regional action plans. The Regional Seas Programme at present includes 12 regions and has some 140 coastal States participating in it (1), (2).

One of the basic components of the action plans sponsored by UNEP in the framework of the Regional Seas Programme is the assessment of the state of the marine environment and of its resources and of the sources and trends of the pollution, and the impact of pollution on human health, marine ecosystems and amenities. In order to assist those participating in this activity and to ensure that the data obtained through this assessment can be compared on a world-wide basis and thus contribute to the Global Environment Monitoring System (GEMS) of UNEP, a set of Reference Methods and Guidelines for marine pollution studies is being developed as part of a programme of comprehensive technical support which includes the provision of expert advice, reference methods and materials, training and data quality assurance (3). The methods are recommended to be adopted by Governments participating in the Regional Seas Programme.

The methods and guidelines are prepared in co-operation with the relevant specialized bodies of the United Nations systems as well as other organizations and are tested by a number of experts competent in the field relevant to the methods described.

In the description of the methods and guidelines the style used by the International Organization for Standardization (ISO) is followed as closely as possible.

The methods and guidelines, as published in UNEP's series of Reference Methods for Marine Pollution Studies, are not considered as final. They are planned to be periodically revised taking into account the development of our understanding of the problems, of analytical instrumentation and the actual need of the users. In order to facilitate these revisions the users are invited to convey their comments and suggestions to:

Marine Environmental Studies Laboratory
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which is responsible for the technical co-ordination of the development, testing and intercalibration of Reference Methods.

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- (1) UNEP: Achievements and planned development of the UNEP's Regional Seas Programme and comparable programmes sponsored by other bodies. UNEP Regional Seas Reports and Studies No. 1, UNEP, 1982.
 - (2) P. HULM: A strategy for the Seas. The Regional Seas Programme: Past and Future, UNEP 1983.
 - (3) UNEP/IAEA/IOC: Reference Methods and Materials: A Programme of comprehensive support for regional and global marine pollution assessments. UNEP, 1990.

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1. INTRODUCTION

In 1980, the International Council for the Exploration of the Sea (ICES) formed a working group (WGMS) to examine the use of sediments and suspended particulate matter (SPM) for monitoring contamination in the marine environment. Since then, this group has systematically reviewed and considered the physical, chemical, and biological characteristics of sediments as well as the processes that contribute to their role as a monitoring tool. During these deliberations, it became clear that laboratories in each country represented on the WGMS used different methods for the sampling and chemical analyses of sediments such as the use of different grain size fractions and acid digestion methods for the determination of heavy metals in marine sediments. As a result, the heavy metal data produced in different laboratories in the same country and in different countries was, and still is, mostly incomparable and unverifiable (Loring and Rantala, 1988). Nevertheless, sedimentary environmental decisions have been, and in many countries are still being, made on the basis of these data.

In 1961, the Canadian Department of Fisheries and Oceans initiated a series of environmental geochemical studies to determine the levels, behavior, and dynamics of heavy metals in eastern Canadian estuarine and coastal sediments and suspended particulate matter. For such studies it was necessary to acquire and develop suitable sample collection, preparation techniques, and precise and accurate analytical procedures for the determinations of Al, Be, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Li, Mg, Mn, Na, Ni, Pb, Rb, Si, Sr, Ti, V, and Zn. In addition, procedures were developed to determine carbonates and organic carbon matter which influence the natural distribution of metals in sediments and suspended particulate matter.

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3. SCOPE AND FIELD OF APPLICATION

The reference methods described in this manual are intended for use in marine monitoring programmes. It has been written to provide detailed instructions on the analytical procedures required for environmental workers to acquire precise and accurate geochemical data for making sound environmental decisions.

The general principles of sample collection, field observations, sample preparation, and grain size separation are covered at the beginning of the manual in sections 4, 5, 6. Sampling strategy is covered briefly in section 15. These procedures are not comprehensive and those whose knowledge of them is limited should consult standard texts for further detailed instructions.

The following three sections (7, 8 and 9) of the manual deal with detailed instructions for sample digestion and atomic absorption determinations of total concentrations of major, minor and trace metals in sediments. Hydrofluoric acid (HF) in combination with aqua regia is used in a sealed teflon decomposition vessel immersed in boiling water or in a microwave oven to decompose the samples for all metal determinations except Hg. The use of HF is essential because it is the only acid that completely dissolves the silicate lattices and releases all the metals including associated metals such as Al, Fe, and Li used for normalization. In addition, such total digestion procedures using HF allow for verification of the results by the use of certified reference materials. In the past, many laboratories have used aqua regia or nitric acid decompositions for heavy metal determinations. These types of digestions are neither used nor recommended here because they have been found to yield incomplete, inaccurate, and unverifiable determinations of metals.

For those readers who are concerned about the use of HF in general and who would benefit from visual information on the methods described here, a 20 minute VHS video (PAL, NTSC, and SECAM systems) is available on request from ICES (Palaegade 2-4, DK Copenhagen K, DK) for the price of copying.

Chemical partition of sediments is used to deduce the source and pathways by which the natural and anthropogenic heavy metals have entered the marine environment. Section 10 of this manual details an analytical procedure to estimate the partition of the total metal concentrations in sediments. It is an operationally defined method based on the use of acetic acid to release the proportion of loosely bound metals from such sites as ion-exchange positions, amorphous compounds of Fe and Mn, carbonates, and those weakly held in organic matter. Data from such determinations have allowed us to make some deductions as to the carriers, transport mode, and potential bioavailability of metals (Loring *et al.*, 1983, 1985). However, it is stressed that this is wholly an operationally-defined procedure for which no reference standards exist.

Accurate and precise analytical data for mercury (Hg) is essential because Hg is often a serious contaminant of sediments in many harbors and estuaries. The analytical procedures using flameless atomic absorption for the determination of mercury in sediments are detailed in Section 11.

Two types of sampling techniques are used for collecting sediments from the sea floor: grab sampling which collects surface and near surface sediments and coring which collects a column of the subsurface sediment. In all grab and core operations, a slow approach to the sea floor should be ensured to avoid the creation of "bow wave" that disturbs the sediment-water interface prior to sampling.

4.2.1 Grab sampling of surface sediments

Undisturbed surface sediment samples can provide an immediate assessment of the present levels of contamination in the area in relation to the textural and geochemical characteristics of the sediment. The sampler used must consistently collect relatively undisturbed samples to a required depth below the sediment surface and of sufficient volume to permit subsequent analyses.

Tightly closing grab samplers, of which there are many designs (Bouma, 1969), are usually adequate for studies of the most recently deposited layer. Special steps can be taken to minimize contamination of the sample such as the use of a stainless steel grab sampler with teflon coatings on all surfaces that come into contact with sediments, and polyethylene coated lowering cables. If the sampler is well designed, no loss of the entrapped sediments and water should occur from the grab after recovery from the sea floor. It is especially important to avoid leakage of fine-grained sediments between the sea-surface and the deck, because this will result in erroneous grain size and compositional determinations.

Onboard, the sediments contained in the grab sampler require attention to ensure that essential components, are neither lost nor augmented by contamination through improper handling. The most critical sampling and storage techniques relate to the avoidance of chemical contamination and change in the physico-chemical characteristics of the sediments.

Initially, a visual inspection should be made of the sample by means of the small trap doors on top of the grab to ensure that the sample has been collected in an undisturbed state and to determine if there is water on top of the sample. If water is present, it can be siphoned off with a glass tube or slowly drained so as not to wash the sample unduly.

Once the top of the sediment is exposed, visual estimates of grain size (coarse, medium, fine grained), color (according to the Munsell color chart code), and the relative proportions of the components should be made and recorded. In situ measurements such as Eh or pH can be made by inserting the appropriate electrodes into the sample.

Most fine grained sediments usually have a thin, dark yellowish brown surface layer resulting from the oxidization of iron compounds at the sediment-water interface. Since in most cases this layer represents the material being deposited at the present time, it should be sampled carefully with a non-contaminating utensil such as a plastic spatula. About 1-3 grams for trace metal determinations should be placed in a numbered polyethylene vial, sealed and frozen for transport to the laboratory. After the surface layer has been sampled, the grab can be opened and an additional sample, representative of the subsurface, can be obtained. Observations of this material should include color and textural characteristics. To ensure a representative sample, about 100 grams or more should be collected and placed in a numbered

(a) One sample (1-10 grams) for trace and major metal determination, except for mercury (Hg), and other analyses should be oven dried or freeze dried to a constant weight.

(b) One sample for Hg determinations. Hg is sensitive to drying and requires a separate subsample, oven dried at 60°C or freeze dried to avoid the loss of any volatile Hg. Determination of dry weight by the traditional oven-drying method has in recent years been supplemented, and in some cases superseded by, freeze-drying.

In oven drying, the samples are placed in plastic or teflon containers and put into a drying oven for 24 hours at a temperature of 105°C or 60°C (Hg) to remove their interstitial water. Oven drying at 100-110°C is suitable for preparing the sample for most types of analysis but may cause the loss of some volatile components and may partially destroy the structure of some clay minerals. Accordingly, drying below 80°C is considered suitable for retaining the clay mineral structure and the most volatile components. For obtaining accurate dry weights, samples dried in this way must be corrected for their residual moisture content.

Freeze drying (or lyophilization) is one of the most useful methods for drying sediments prior to most chemical analyses because of the lower risk of losing volatile elemental components and providing a powdery material instead of hard clay aggregates. However, freeze drying, like oven drying, retains soluble sea salts that can interfere with some major element analyses and preclude some measurements of physical structure.

NOTE: Recent studies (Bartlett and James, 1980, Thompson *et al.*, 1980, and Kersten and Forstner, 1987) indicate that air, oven, and freeze drying all introduce physical and chemical changes in the composition of the original sedimentary material after it has been removed from its in situ environment. Most of the changes relate to oxidation/reduction changes, and affect the proportion of metals weakly held in the sediments. For example, Kersten and Forstner (1987) found that oven drying and freeze drying, carried out separately under vacuum, change the original associations of the metals amongst the various sedimentary components. Since trace metal concentrations are relatively high in most sediments, such changes are most likely insignificant in relation to other errors in total trace metal determinations. In any event, such effects can be minimized by careful sampling, storage, and use of the material.

5.1.4 Water content

Fresh sediment samples contain 30 to 95% by weight of water. In addition to the requirement for constant weight dry samples, the water content should be measured because it allows a salt content correction factor to be calculated in sediments of high water content, and allows one to go from measurements of sedimentation rates (mm year^{-1}) to mass accumulation rates when radiochemical analyses are performed.

5.1.5 Determination of water content in wet samples (Oven drying).

- (a) Weigh out accurately 1 to 10 grams of the wet sample (x grams) into a plastic or teflon weighing container that has been dried at 105°C and preweighed;
- (b) Place in drying oven (pre-heated to 105°C) for 24 hours;

ensure that there is no contamination of sediments by the sea-water and that there are no chloride-induced interferences in the chemical analyses.

- (a) Transfer 10 to 20 grams of dry sample to a 1 liter polypropylene centrifuge bottle;
- (b) Disperse it by shaking for 30 minutes with 1 liter of water (distilled and deionized water);
- (c) Centrifuge the suspension at 2000 rpm until clear;
- (d) Siphon the water off, repeating until the supernatant is chloride free (tested by adding AgNO_3 to a small water sample which precipitates the chloride as AgCl_2);
- (e) Transfer the sediment to an evaporating dish and dry in the oven at 105°C ;
- (f) Crush the dried sample in an agate mortar, mix well to avoid selective crushing, and store in air-tight vials until required.

5.1.9 Storage of samples

After drying, the various sub-samples are placed in a desiccator until cool, and stored in air tight plastic vials until required for future use.

6. SEDIMENTOLOGICAL ANALYSES

Sedimentological analyses involve procedures for determining the granulometric and mineralogical composition of the sediments. Since this report is concerned primarily with chemical analyses, only the outlines of the procedures for grain size determinations are given below and the reader is referred to the standard textbooks on the subject for details.

6.1 Grain size separation

The chemical composition of marine sediments changes with the grain size and mineralogical composition. Usually, the trace metal concentrations increase with decreasing grain size of the material. This is because the host minerals of the elements and the surface area of the particles making up the sediment change with grain size. In addition, regional comparisons of elemental concentrations can only be made by using texturally equivalent sediments and/or size fractions. It is, therefore, often necessary to normalize for the "grain size effect" and sometimes to determine the elemental concentrations in different size fractions of the sediments.

6.1.1 Determination of sand and mud size material

Determination of the amount of sand and mud size material by weight is essential for the basic classification and identification of the sediment texture. The general scheme for the separation of the different grain size fractions is shown in Figure 2.

- (a) Use a preweighed dried sample to determine the amount of sand ($>63\mu\text{m}$) and mud ($<63\mu\text{m}$) size material in the sediment sample;

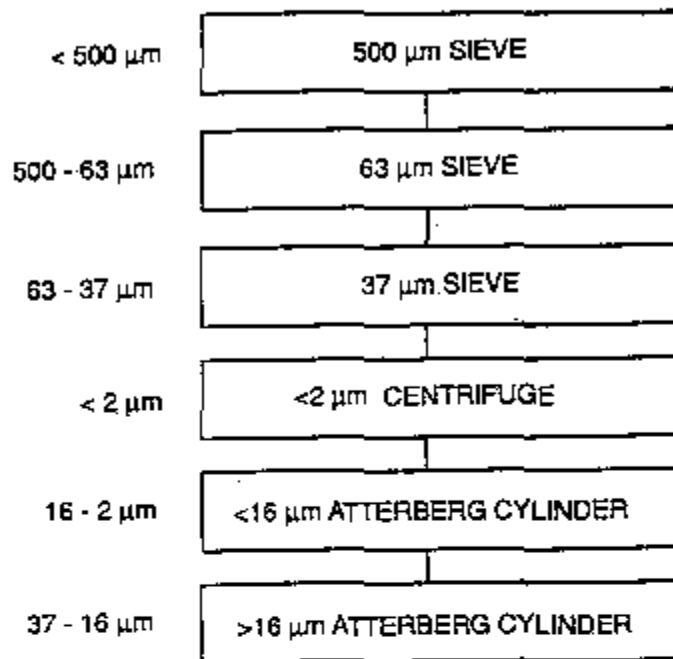


FIGURE 2: General Scheme for Grain Size Separation.

- (e) Dry each fraction at 105°C, cool in a desiccator, and weigh (except the one from the >500μm sieve);
- (f) Resieve the dry >500μm fraction through a 2000μm sieve to remove rock fragments >2mm and weigh;
- (g) Calculate the dry weight percentages for each size fraction from the equation:
Size fraction = Wt. of fraction / wt of sample X 100;
- (h) Retain the liquid passing through the 37μm sieve;
- (i) Pour into a centrifuge bottle, and make up to 1 liter with 0.16N NH₄OH as the dispersive agent;
- (j) Shake mechanically for 30 minutes (an ultrasonic probe could be used instead of NH₄OH to disperse the sample);
- (k) Separate the <2μm fraction by centrifuging (the centrifuging time is calculated from Stoke's law, Tanner and Jackson, 1947). If a centrifuge is not available, the <2μm fraction can be separated in a beaker according to the sampling times shown in Table 1;
- (l) Siphon the <2μm material off and store in centrifuge bottles;

8.1.6 Sample size

The size of sample required depends mainly on the expected metal concentrations. In general, a 0.1 gram sample is used for the major elements and a 1 gram sample is used for trace metal determinations if only flame AAS is available (Section 9.5). A 200 mg sample containing normal amounts of major and trace metals, however, has been found to be sufficient for most metal concentrations if the sample is homogeneous and graphite furnace AAS is available. It would be preferable to make only one decomposition for all elements using 0.1-0.3g sample size and adjusting the dilutions (Section 9.5) accordingly. Certain trace metals occurring in very low concentrations may require larger sample sizes.

Maximum sample size used in the microwave decomposition is 200 mg. Larger samples may be feasible although small samples are best suited for microwave heating. To obtain more concentrated solutions, the final volume can be reduced from 100 ml to 50 ml. In that case, only 3 ml of HF and 2.8 g of H_3BO_3 should be used for the decomposition.

8.2 Total decomposition procedure

- (a) Accurately weigh 100-1000 mg (100-200 mg for microwave heating) of finely ground sample;
 - (b) Transfer to a teflon bomb;
 - (c) Add 1 ml of aqua regia (HNO_3 : HCl , 1:3 w/v);
 - (d) Add 6 ml of HF very slowly to avoid excessive frothing;
 - (e) Close the bomb tightly and submerge in boiling water for a minimum of 1 hour;

OR place the bombs (4) in the microwave pressure cooker; place the cooker along with a beaker containing 50 ml water in the microwave oven; heat for 70 seconds at full power (700w);
- Some Cr, Ti and Ba bearing minerals are difficult to dissolve and require 2 h in boiling water or an additional 5 min. at med/low power in the microwave oven.
- (f) Remove the bomb from the heat source and cool it to room temperature in cold water or an ice bath;
 - (g) Weigh 5.6 g of H_3BO_3 and transfer into a 100 ml polypropylene volumetric flask;
 - (h) Add 20 ml of H_2O and shake briefly;
 - (i) Remove the bomb from the cooling water, and dry it;
 - (j) Open the bomb, (be sure to wipe off any water found on the outside of the sealing area) and transfer the contents into the 100 ml polypropylene flask;

9.1 Apparatus and equipment

Atomic absorption spectrophotometer.
Hollow cathode lamps, and EDL lamps.
Pyrolytically coated and uncoated graphite tubes.
Digital diluter.
Polystyrene disposable culture tubes.
Eppendorf digital pipettor 100-1000 μ l.
Various pipettes.
Volumetric flasks, polypropylene and glass.

9.2 Calibration standards

Single-element standards can be used, but for convenience, a combined stock solution can be prepared for some metals. Single-element standards are prepared for Si, Ti, Ba, Be, Cr, Sr, Rb and V. Multi-element standards are prepared for Al, Ca, Fe, K, Mg, Na, Cd, Co, Cu, Li, Ni, Pb, and Zn. Single or multiple element stock solutions are prepared from 1000 μ g/ml standards. The 1000 μ g/ml standards are either prepared in the laboratory or obtained commercially.

To compensate for matrix effects between samples and standards, a decomposition blank is required for preparing the working standards and should contain 1 ml of aqua regia, 6 ml concentrated HF, and 5.6 g H_3BO_3 /100 ml.

In addition, KCl is added in solution or as a solid to some of the working standards and sample solutions to suppress ionization during flame absorption.

Details for preparing stock solutions are usually found in the instructions provided by the manufacturer of the atomic absorption equipment.

9.2.5 Ba single element standard

Dilute the 1000 $\mu\text{g/ml}$ stock solution to obtain working standards of 0.1-2.0 $\mu\text{g/ml}$ Ba.

Make up the working standards in the decomposition blank. Add solid KCl to each standard so that the final concentration is 1500 $\mu\text{g/ml}$ K.

9.2.6 Be single element standard*

Dilute the 1000 $\mu\text{g/ml}$ stock solution to obtain working standards of 5-30 $\mu\text{g/l}$ Be in the decomposition blank.

**In preparing Be standards, it is advisable to use commercially available stock solutions because beryllium dust is extremely hazardous.*

9.2.7 Cr single element standard

Dilute the 1000 $\mu\text{g/ml}$ stock solution to obtain working standards of 0.1-1.5 $\mu\text{g/ml}$ Cr in the decomposition blank.

Further dilute the working standards with H_2O for GFAAS determinations.

9.2.8 Rb single element standard

Dilute the 1000 $\mu\text{g/ml}$ stock solution to obtain working standards of 0.2-3.0 $\mu\text{g/ml}$ Rb in the decomposition blank containing sufficient K added to match the sample K concentrations.

The reason for careful matching is that the absorption of Rb is suppressed by the decomposition blank solution and enhanced by K. The enhancement by K is progressive to about 600 $\mu\text{g/ml}$ K, above which suppression by K occurs. Thus the addition of excessive amount of K results in a vastly suppressed absorption signal and is not recommended. Enhancement by Na is, however, small. For example, when 200 $\mu\text{g/ml}$ of Na and K are added to a 1 $\mu\text{g/ml}$ Rb standard in the decomposition blank, the enhancement is only about 2% more than in 200 $\mu\text{g/ml}$ K. Since the determination of Rb is highly dependent on K concentration, it is first necessary to determine the K content of the samples and match it to the standards for the most accurate determinations. Since the absorption of Rb is linear to about 3 $\mu\text{g/ml}$ Rb for a particular K concentration, several standard curves with varying K concentrations can be drawn by using just one standard in each case for fast but less accurate Rb determination. The Rb concentration can then be read from the standard curve having the K concentration closest to that of the sample. When large numbers of samples are analyzed, therefore, it may not be practical to match the concentration of K in each standard, but the Rb can be interpolated from other standard curves.

USGS reference materials are available from: J.S. Kane, U.S. Geological Survey, Reston, VA 22092, USA.

IAEA CRM's (contaminated and deep-sea marine sediments) are available from: International Atomic Energy Agency, Analytical Quality Control Services, Agency's Laboratories Seibersdorf, A-1400 Vienna (Austria) and/or IAEA-MEL/MESL, 19, avenue des Castellans, MC 98012 Monaco Cedex.

9.5 Sample dilutions

Flame AAS may be used to determine precisely and accurately the major and trace elements in sample solutions providing the concentrations are adjusted so that they fall within the linear portion of the calibration curve and are confirmed by the use of reference solutions derived from the dissolution of CRM's. For most major elements this requires a further dilution of the sample solution (Table 2). A KCl solution is often used as a diluent not only to adjust the concentrations to the optimum range but also to suppress ionization of certain metals (Table 2). Such dilutions are made rapidly by using an adjustable diluter and disposable polystyrene culture tubes.

Table 2 shows that the 0.1 gram sample solution from the teflon bomb decomposition is initially diluted to 100 ml (1000x dilution).

TABLE 2
Sample Dilution Scheme for Flame AAS Analyses

Sample Wt. grams	Dilution	Element
0.1	1000X	Mn, Si
	1000X in 1500 $\mu\text{g/ml}$ K	Ba, Sr, Ti
	20000X in 1500 $\mu\text{g/ml}$ K	Al, Ca, Fe, Mg, Na
	20000X in 1500 $\mu\text{g/ml}$ Na	K
1.0	100X	Be, Cd, Co, Cr, Cu Li, Ni, Pb, Rb, V, Zn

9.5.1 Solutions for major and some minor element determinations

- Mn and Si are determined directly without any other dilutions.
- Solid KCl is added to separate aliquots to give a K concentration of 1500 $\mu\text{g/ml}$ and these are analyzed for Ba, Sr, and Ti.
- For the determinations of Al, Ca, Fe, Mg, and Na; a further 20X dilution is made to give the desired dilution factor of 2×10^4 in the KCl (1500 $\mu\text{g/ml}$ K) matrix. A similar dilution is also made for the determination of K by substituting NaCl as the diluent.

Table 3. For other instruments, readers should consult their own manuals for the correct instrumental settings.

9.7 Interferences

Matrix interferences for major and trace elements are reduced by diluting the sample solutions in such a way as to adjust the concentrations to the linear portion of the absorbance curve.

Ionization is controlled by additions of 1500 µg/ml K or Na to standards and samples (Section 9.5; Table 2). For example, ionization in Ba and Sr determinations is controlled by adding 1500 µg/ml K to samples and standards.

Chemical suppression of elements such as Si and Al on Ca and Mg absorption is avoided by the use of nitrous oxide-acetylene flame. This eliminates the need for lanthanum which is essential in an air-acetylene flame.

Standards for Rb and V require special attention as discussed under standard preparation (Sections 9.2.8 and 9.2.10).

Molecular absorption is corrected by the Deuterium Background Corrector in Co, Ni, and Pb determinations.

GFAAS should be used for Ni if it is available. FAAS determination of Ni is prone to matrix interferences: use of a deuterium background corrector produces low results but not using it produces high results. Use of alternative calibration standards (section 9.3) will partly compensate for such influences.

No interferences have been observed for Be, Cu, Li, Mn, Si, and Zn in a fluoboric-boric acid mixture.

9.8 Graphite furnace determinations

GFAAS determinations require the use of L'vov platforms, preferably automatic sample introduction, optimization of instrumental parameters, background corrections for Cd, Co, Ni, and Pb, and correct application of appropriate reference materials.

Low levels of Al, Cd, Co, Cr, Cu, Ni, Pb, and V are determined by GFAAS.

9.8.1 Calibration standards

Calibration standards are diluted from stock standard solutions to the appropriate range in the same reagent matrix as the sample.

9.8.2 Use of L'vov Platforms

A L'vov platform placed in a graphite tube permits the atomization of the sample under nearly isothermal conditions. This results in the reduction of interferences and permits direct comparison with aqueous standards (Sturgeon et al., 1982). L'vov platforms for Cd and

(b) **Charring:** Charring temperature, ramp and hold times must be optimized to avoid loss of metals during this cycle.

(c) **Atomization:** The fastest possible ramp time to atomization temperature should be used. The atomization temperature is determined experimentally. The gas interrupt is not usually required.

Instruments having a maximum power mode feature such as the Perkin Elmer HGA-500 require temperature control calibration. During calibration, be sure to press the manual temperature button long enough, while adjusting the calibration control. With the platform, the time required to adjust the calibration control at 1600°C could be as long as 30 - 40 seconds.

The GFAAS parameters for the HGA-500 graphite furnace are shown in Table 4.

TABLE 4
GFAAS Parameters

Metal	Platform Type	Background Corrector	Dry (°C)	Char (°C)	Atomize (°C)	Burn out (°C)	Cooling (°C)
Al	pyrolytic	OFF	270	1500	2400	2700	20
Cd	non-pyrolytic	ON	270	400	1600	2700	20
Co	pyrolytic	ON	270	1000	2700	2700	20
Cr	pyrolytic	OFF	270	900	2400	2700	20
Ni	pyrolytic	ON	270	1000	2700	2700	20
Pb	non-pyrolytic	ON	270	550	1800	2700	20
Cu		OFF	120	900	2100	2700	-
V		OFF	120	1500	2700	2700	-
Ramp(s)			10	20	max power	1	1
Hold(s)			20	20	3	3	15

Table Type: Pyrolytic. Sample volume: 20 µL. Argon flow during atomization: 50 ml/min. Gas interrupt mode is used for low concentrations of Cd and Pb.

9.9 Interferences

Sample solutions for Al, Cr and V determinations are diluted with water (Al 500X, Cr 10X, V 10X) prior to GFAAS determinations. This is important for Cr as, in our experience, Cr recoveries using GFAAS can be reduced as much as 60% due to suppression of Cr absorption by matrix elements unless the solutions are diluted 10X with water.

Interferences by matrix elements are reduced significantly by using the L'vov platform.

TABLE 6
Major and Minor Constituents of Standard Reference Materials

Oxide	PACS-1		W-2		BIR-1		DNC-1	
	%	sd	%	sd	%	sd	%	sd
Al ₂ O ₃	<i>12.19</i>	<i>0.12</i>	<i>14.83</i>	<i>0.28</i>	<i>15.19</i>	<i>0.19</i>	<i>17.94</i>	<i>0.24</i>
	12.23 ^c	0.22	15.35 ^{cs}	0.23	15.35	0.51	18.30	0.49
CaO	<i>2.84</i>	<i>0.01</i>	<i>10.98</i>	<i>0.06</i>	<i>13.35</i>	<i>0.19</i>	<i>11.40</i>	<i>0.20</i>
	2.92	0.13	10.87	0.29	13.24	0.29	11.27	0.22
Fe ₂ O ₃	<i>6.98</i>	<i>0.04</i>	<i>10.60</i>	<i>0.09</i>	<i>11.14</i>	<i>0.12</i>	<i>9.84</i>	<i>0.08</i>
	6.96	0.12	10.74	0.23	11.26	0.23	9.93	0.14
K ₂ O	<i>1.51</i>	<i>0.02</i>	<i>0.60</i>	<i>0.01</i>	<i>0.012</i>	<i>0.004</i>	<i>0.20</i>	<i>0.00</i>
	1.50	0.09	0.63	0.02	0.027	0.010	0.23	0.02
MgO	<i>2.48</i>	<i>0.02</i>	<i>6.24</i>	<i>0.05</i>	<i>9.44</i>	<i>0.13</i>	<i>9.96</i>	<i>0.19</i>
	2.41	0.09	6.37	0.18	9.68	0.28	10.05	0.33
Na ₂ O	<i>4.45</i>	<i>0.03</i>	<i>2.18</i>	<i>0.01</i>	<i>1.77</i>	<i>0.04</i>	<i>1.87</i>	<i>0.03</i>
	4.40	0.11	2.14	0.12	1.75	0.11	1.87	0.09
SiO ₂	<i>55.27</i>	<i>0.19</i>	<i>52.47</i>	<i>0.50</i>	<i>47.94</i>	<i>0.45</i>	<i>47.16</i>	<i>0.35</i>
	55.70	0.50	52.44	0.64	47.77	0.51	47.04	0.64
TiO ₂	---		<i>1.06</i>	<i>0.01</i>	<i>0.94</i>	<i>0.03</i>	<i>0.48</i>	<i>0.01</i>
			1.06	0.03	0.96	0.03	0.48	0.02

c = Certified values for PACS-1 (NRCC)

cs = Consensus mean values for W-2, BIR-1, and DNC-1 (Gladney and Roelandts, 1988a).

Numbers in *italics* obtained by Loring and Rantala, 1992 (W-2, BIR-1, and DNC-1 from Flanagan, 1984).

9.12 Comparison of microwave and conventional (Boiling Water) Teflon bomb digestion.

For this experiment, three sediment samples containing natural levels of metals were digested (HF + aqua regia) in triplicate using 0.2 g samples by both 70 second microwave and 1 hour conventional heating methods.

Table 8 compares the results obtaining using the combined analytical scheme (Table 5) by the two methods.

The data show that the microwave mean concentrations and precision compare well with those obtained for the conventional digestion.

TABLE 8
Comparison of Metal Determinations from Conventional (Boiling Water) and Microwave Digestions.

Element	Sample A sd		Sample B sd		Sample C sd	
Al (%)	7.10 ^c	0.14	7.16	0.19	7.53	0.09
	7.10 ^m	0.11	7.19	0.08	7.58	0.20
Fe (%)	3.69	0.01	3.36	0.01	3.84	0.01
	3.68	0.01	3.29	0.01	3.79	0.07
Cd (mg/kg)	0.11	0.01	0.10	0.02	0.27	0.00
	0.11	0.01	0.09	0.00	0.27	0.01
Cr	84	0.6	72	1.7	89	2.3
	82	2.1	68	1.0	85	1.5
Cu	27	0.6	24	0.6	36	0.6
	27	1.0	23	1.0	37	1.2
Li	61	0.0	49	0.6	60	0.6
	61	0.6	49	0.6	60	0.6
Mn	446	3.8	478	0.6	415	1.0
	442	1.2	463	1.5	414	6.7
Pb	26	0.6	32	2.1	40	0.6
	25	0.0	28	0.6	39	0.0
Zn	92	1.5	85	2.0	127	1.0
	92	1.2	83	1.2	126	2.0

c - Conventional method: 1 hour bomb digestion (HF + aqua regia) in boiling water (n=3).

m - Microwave method: 70 second bomb digestion (HF + aqua regia) in microwave oven (n=3).

10.1.2 Labware

Polypropylene centrifuge tubes, 30 ml with caps
Polypropylene narrow mouth bottles.
Glass volumetric flasks, 50 ml.
Funnel.

10.1.3 Reagents

Glacial acetic acid [HOAc], 25% v/v (ACS analytical grade).
Deionized reverse osmosis water.

10.2 Extraction procedure

- (a) Place a portion of dry sample in an agate mortar. Do not grind it. Simply crush the lumps;
- (b) Weigh 2 grams of sample and transfer it into a propylene centrifuge tube;
- (c) Weigh the tube + the sample and record the weight;
- (d) Add 25 ml of 25% v/v HOAc;
- (e) Cap the tube and shake slowly in a mechanical shaker for 6 hours;
- (f) Balance the centrifuge tubes and centrifuge for 10 minutes at 2500 RPM or until the supernatant is clear;
- (g) Pour the supernatant HOAc into a 50 ml volumetric flask;
- (h) Wash the sediment with 10 ml of water and shake the tube briefly on the shaker;
- (i) Separate the wash water by centrifuging and add it to the flask;
- (j) Rinse the funnel and make up the HOAc solution to a volume of 50 ml;
- (k) Dry the tube containing the residue in the oven at 105°C and place in the desiccator to cool;
- (l) When the tube reaches room temperature, weigh it and calculate the percent by weight contribution of the residual fraction;
- (m) Transfer the dry residue to the mortar and use a portion of the ground up sample for the HF teflon bomb decomposition to determine the trace metals held in the acid insoluble or detrital fraction of the sediments;

- (e) No platform is used for Cu which is determined using a pyrolytically coated tube.

10.3.6 L'vov platform conditioning for Cd

It was found that the platform had to be conditioned for the Cd determination in the acetic acid matrix to ensure reproducible results. Reproducible results can be obtained by running a conditioning solution made up of a HOAc sediment leachate (2g/50 ml) at the beginning of the analyses and between each sample and standard.

10.3.7 Furnace control program steps

The furnace controller programs used are shown in Table 4. In addition, two other steps are used.

- (a) The residual matrix is removed by a 3 sec firing at 2700°C and the platform is cooled for 15 sec at 20°C before the next sample is introduced into the furnace.
- (b) It is also necessary to lower the atomization temperature for Cd from 1600°C in the H₃BO₃ matrix to 1100°C in the acetic acid matrix.
- (c) Internal argon flow is reduced to 50 ml/min during atomization. Gas interrupt mode is used for low Cd concentrations.

10.4 Calculations of non-detrital (acid soluble) and detrital (acid insoluble) contributions

The total metal concentration is the sum of the acetic acid soluble and residual contributions.

For example: Zn.

Let:

Sample wt. for HOAc leach	=	2.000g
Wt. of HOAc residue	=	1.800g
Wt. of residue for decomposition	=	0.300g
Vol. of flask for HOAc solution	=	50 ml
Vol. of flask for decomposition solution	=	100 ml
Concentration of Zn in HOAc solution	=	0.20µg/ml
Concentration of Zn in decomposition solution	=	0.25µg/ml
Non-detrital contrib. of Zn = 50/2.000 X 0.20	=	5µg/g
Detrital contrib. of Zn = 1.800/2.000 X 100/0.3 X 0.25	=	75µg/g

Therefore:

$$\text{Total Zn concentration} = 5\mu\text{g/g} + 75\mu\text{g/g} = 80\mu\text{g/g}$$

11.2 Sample preparation

- (a) Oven dry the sediment at 60°C;
- (b) Crush lumps and grind lightly to homogenize the sample;
- (c) Weigh accurately 500 mg of sample (less if the sample might contain > 0.2 mg Hg / kg). Use samples smaller than 500 mg if excessive frothing occurs during aerating;
- (d) Transfer weighed sample to BOD bottle;
- (e) Add 10 ml of concentrated HNO₃ followed by 20 ml of concentrated H₂SO₄. Do not stopper;
- (f) Place the BOD bottle in the water bath and digest for 1 hour at 60°C;
- (g) Remove from the water bath and add 150 ml of water, insert the stopper, and place in freezer or cold water until room temperature.

NOTE: Before adding acid to any sample, the blank solution must be analyzed for Hg to assure that the reagent blank is not excessively high. Another blank should be run with the samples.

11.3 Preparation of standards

11.3.1 Hg: 1000 µg/ml stock solution

- (a) Dissolve 0.1354 g of mercury (II) chloride into 100 ml of 1N sulfuric acid;
- (b) From this solution prepare a 10 µg/ml solution in 5% HNO₃ and 0.01% K₂Cr₂O₇ (Feldman, 1974). The 10 µg/ml solution prepared in this way is stable for several months.

11.4 Working standards

Once a week, dilute the 10 µg/ml Hg solution to obtain a 0.1 µg/ml solution in 5% HNO₃ and 0.01% K₂Cr₂O₇.

Prepare the working standards for each batch of samples by dispensing 0.10 -1.00 ml of the 0.1 µg/ml Hg solution from a digital pipetter into BOD bottles. Add the same volume of reagents as to the samples. Digestion of the standard is not normally necessary although it may be safer to put it through the same procedure as the samples.

The Walkley-Black method utilizes exothermic heating and oxidation with potassium dichromate and concentrated H_2SO_4 of the sample, followed by the titration of excess dichromate with 0.5N ferrous ammonium sulfate solution to a sharp, 1 drop, end point. Oxidation of Cl^- can be prevented by the use of Ag_2SO_4 in the digestion mixture.

12.1 Apparatus and reagents

12.1.1 Apparatus

2-50 ml burette with 0.1 ml graduations.
Magnetic stirrer.
500 ml Erlenmeyer flasks.

12.1.2 Reagents

85% H_3PO_4 .
Solid NaF.
Concentrated H_2SO_4 with Ag_2SO_4 (dissolve 2.5 g Ag_2SO_4 in 1 liter of H_2SO_4).
Standard 1N $K_2Cr_2O_7$ solution (dissolve 49.04 g of $K_2Cr_2O_7$ in water; dilute to 1 liter).
0.5N Ferrous solution (dissolve 196.1 g of $Fe(NH_4)_2SO_4 \cdot 6H_2O$ in 800 ml of water containing 20 ml of concentrated H_2SO_4 ; dilute to 1 liter).
Diphenylamine Indicator (dissolve approximately 0.5 g of reagent grade diphenylamine in 20 ml of water and 100 ml of concentrated H_2SO_4).

12.2 Determination of organic carbon

- (a) Place 0.5 grams of dried and sieved (200 μm sieve) sediment sample in a 500 ml Erlenmeyer flask;
- (b) Add exactly 10 ml of 1 N $K_2Cr_2O_7$ solution by burette and 20 ml of concentrated H_2SO_4 with Ag_2SO_4 and mix by gently rotating the flask for about 1 minute;

NOTE: This should be done carefully, to insure complete mixing of the reagents with the sediment, while avoiding splashing the sediments onto the sides of the flask out of contact with the reagents.

- (c) Allow the mixture to stand for 30 minutes;
- (d) A standardization blank without sediment should be run with each new batch of samples;
- (e) After 30 minutes, add 200 ml distilled water, 10 ml of 85% H_3PO_4 , and 0.2 g NaF;
- (f) Add 15 drops of the diphenylamine indicator to the sample flask;
- (g) Back titrate the solution with the 0.5 N ferrous ammonium sulfate solution to a one-drop end point (brilliant green).

For a simple determination of calcium carbonate (CaCO_3), the sediment is placed in a pre-weighed stoppered flask and treated with HCl. By adding excess HCl to CaCO_3 , a certain volume of CO_2 is evolved, while an equal volume of air is expelled. The loss of weight due to the escape of air expelled by the evolved CO_2 is determined. As both CO_2 and air follow the Boyle-Gay Lussac Law, and weights are determined instead of volumes, the temperature and pressure have no influence on the analysis, assuming that these quantities do not change between weighings.

13.1 Apparatus and reagents

13.1.1 Apparatus

Conical flask, 250 ml

Rubber stopper fitted with a glass tube filled with CaCl_2 to remove water vapour and plugged at both ends with cotton. Another similar tube is attached to the first tube by means of plastic tubing. This tube is used to ensure that outside moisture does not enter the main tube.

Glass vials: 7 ml

Desiccator

Analytical balance

13.1.2 Reagents

HCl 4N: dilute 330 ml of concentrated HCl to 1 litre with water.

CaCO_3 : reagent grade, oven dried and stored in the desiccator.

13.2 Determination of carbonate

- (a) Transfer 1 g of oven dry ground sediment into a 250 ml conical flask (see A in Figure 3);
- (b) Place vial D filled with 5 ml of 4N HCl into the flask;
- (c) Close the flask with a rubber stopper containing tube B filled with CaCl_2 ;
- (d) Determine the total weight;
- (e) Mount tube C also filled with CaCl_2 on top of tube B with the aid of a piece of plastic tubing;
- (f) Tilt the flask so that the HCl in vial D is poured out onto the sediment sample;
- (g) During the next 2 hours, swirl the contents of the flask occasionally so that the acid is in contact with the sediment;

13.3 Precision of carbonate determinations

Replicate analyses (6) of a sample with an average of 6.84% CaCO_3 gave a standard deviation of $\pm 0.18\%$ (coefficient of variation of 2.6%).

14. SUSPENDED PARTICULATE MATTER (SPM)

Samples of suspended particulate matter are collected to determine their concentration and distribution in the water column as well as their inorganic and organic composition.

Suspended particulate matter is commonly defined in terms of pore size of the filter being used. Since the build up of particles on a filter modifies the effective pore size of the filter, the material retained on the filter includes additional particles smaller than the original pore size. In practice, suspended particulate matter is defined operationally as that which is retained by the type of filter being used.

Suspended particulate matter in this report is defined as that retained by Nuclepore 0.4 micron (μm) polycarbonate filter membranes.

Nuclepore filters are widely used for gravimetric and chemical determinations. They have well defined pore sizes that give them a relatively precise cutoff in the size of particles that they retain. The polycarbonate composition of the filters is relatively metal free and hydrophobic which makes them easy to tare and reweigh after sample collection. The major disadvantage of the Nuclepore filters is that they clog at relatively low loadings which limits the amount of material that can be collected.

The collection of suspended particulate matter involves procedures for the preparation of the filters, collection of SPM samples, washing of the filter to remove salt, and reweighing. The following subsections contain a summary of these procedures.

For detailed instructions, the reader should consult the report by Yeats and Brugmann (1990) on the collection of SPM for gravimetric and trace metal analysis.

14.1 Filter preparation

All preparation should be done in as dust free an environment as possible because the filters tend to build up a static charge and thus attract particles from the air. A clean room is the best environment for handling the filters, but a laminar flow clean bench is sufficient. It is essential to use an anti-static source to remove any static charge immediately before weighing because of the static charge build-up.

For trace metal analyses, the filters should be soaked for 24 hours in 2N HNO_3 (Merck, pro analysi) and then rinsed several times in Milli-Q water. The filters are stored in polycarbonate petri dishes that have been rinsed, then soaked in 6N HCl and rinsed again and then dried in a microwave oven. When the filters have returned to room temperature they can be transferred with plastic tweezers to a microbalance capable of weighing an ~ 20 mg filter to ± 0.01 mg. After weighing, the filters should be stored flat in individual numbered precleaned petri dishes because they will have to be loaded onto flat filter holders.

14.2.2 On-line filtration

For the lower SPM concentration, an on-line direct filtration from the Go-Flow or Niskin bottle is used. In this procedure, the filter in its holder is attached to the modified teflon drain spigot of the Go-Flo sampler with a piece of clean silicon tubing and nitrogen pressure (maximum ~0.8 atm) is applied by attaching the pressure line to an adapter designed to hold the nitrogen line. The sample is filtered until the filter clogs or all of the water sample has been passed through the filter. To inhibit particle settling, the water bottles are occasionally inverted during sampling.

14.3 Filter washing

While still in their holders, each filter is then washed by attaching the holder to the off-line separatory funnel as described in section 14.2.1 and rinsed with two 50 ml aliquots of filtered (0.2 μ m) Milli-Q water while applying nitrogen pressure. The washed filters are dried for 12 hours at 60 °C in an oven or in a microwave oven, cooled in a desiccator, and then reweighed to obtain the weight of the SPM retained on the filter. After weighing, the filters are stored flat in individual numbered precleaned petri dishes until required for chemical analyses. The SPM concentration in mg/l in the water column is calculated from the weight of the SPM retained on the filter and the volume of water filtered.

14.4 Total HF decomposition of suspended particulate matter

The Nuclepore filters are decomposed in Teflon bombs in a manner similar to sediments, but with smaller amounts of reagents. The filters themselves are not decomposed (Rantala and Loring, 1977, 1985). The number of steps that are followed will depend on the nature and extent of the investigation. It is recommended that, at least, the total trace metal concentrations except chromium (Cr) be determined for each sample. Chromium cannot be determined accurately in the SPM because of the high content of this element in Nuclepore filters (Yeats and Dalziel, 1987).

14.5 Apparatus and reagents

For the suspended particulate matter decomposition, the same teflon bombs and heating equipment are used as described in Sections 8.1.1 and 8.1.2.

14.5.1 Laboratory equipment

- Mechanical shaker.
- Microbalance (readability 0.01 mg).

14.5.2 Labware

- Polypropylene volumetric flasks, 25 ml.
- Polypropylene narrow mouth bottles.
- Polypropylene funnel.
- Plastic tweezers.

14.6.1 A preferred alternative method for low concentrations of metals

After step (c) above

- (a) Weigh a small precleaned polypropylene bottle;
- (b) Add 0.5 g of boric acid and 1 ml of water into the bottle;
- (c) Transfer the contents of the bomb (except the filter) into the bottle; Rinse well and add to the bottle;
- (d) Add H₂O until the weight of the solution equals 10.6g (10 ml);
- (e) Shake the bottle to complete the dissolution;
- (f) Analyze the solutions for trace metals by flame or graphite furnace AAS.

14.7 Atomic absorption analyses of SPM

FAAS is used to determine: Si, Ca, Fe, Mg, Mn, Na, K, Cu, Li, and Zn.

GFAAS is used to determine: Al, Cd, Ni, Pb and also Cu when it is too low in concentration to determine by FAAS.

14.7.1 Apparatus

The same as for sediments.

14.7.2 Calibration standards

- (a) Calibration standards are diluted from commercial 1000 µg/ml stock solutions.
- (b) Final working standards are prepared in the same matrix as the sample to be analyzed. i.e. decomposition blank, ultra high purity KCl, NaCl, or H₂O.
- (c) Alternatively, certified reference materials (CRMs) may be used for calibration. A minimum of 3 sediment or rock CRMs should be chosen to cover the expected concentration range. For such a calibration, 3-10 mg of each CRM is decomposed in the same manner as the SPM samples and a fourth CRM is used as an accuracy check.

14.7.3 Reference Materials

Certified reference materials (CRMs) are used to confirm the accuracy when calibration standards are prepared from 1000 µg/ml stock solutions. To prepare the CRM standards: 3-10 mg of each CRM is decomposed in the same manner as the SPM samples. Metal concentrations in the CRM solutions should be in the concentration range of the SPM solutions.

14.8 Acetic acid extraction of SPM

The chemical technique to partition the particulate metals into their non-detrital and detrital phases involves the leaching of the particulate matter on Nuclepore filters with 25% v/v acetic acid in a modified Millipore Sterifil vacuum filtration apparatus (Rantala and Loring, 1985). The residue remaining on the filters is decomposed with a combination of ultra-high purity hydrofluoric acid and aqua regia in the teflon bombs.

14.9 Apparatus and reagents

14.9.1 Extraction apparatus

Polycarbonate Millipore Sterifil vacuum filtration funnel and receiver flask attached to a polypropylene Millipore Swinnex-47 mm filter holder base* (Figure. 4).

Silicone tube containing a short glass rod which is attached to the filter outlet.

Vacuum pump

*It is necessary to replace the red silicone O-ring with a teflon O-ring because the silicone O-ring has been found to contaminate the filtrate with Zn. In addition, some filter supports have been found to contain metallic particles that release Zn during leaching. To prevent contamination from this source, the supports should be examined for such particles with a microscope and be replaced if particles are found to be present.

14.9.2 Labware

Glass volumetric flasks, 10 ml.

Polypropylene narrow mouth bottles.

Polypropylene funnel.

Plastic tweezers.

14.9.3 Reagents

Glacial acetic acid [HOAc] 25% v/v ultra-high purity.

De-ionized reverse osmosis water.

14.9.4 Sample size

The amount of SPM sample required for precise and accurate determinations of the elements will depend on their concentration in the SPM. A minimum of 3 mg (dry weight) is usually required under this procedure to partition most of the particulate metals into their non-detrital and detrital phases at their natural background levels. Samples smaller than 3 mg can be used, but it may not be possible to determine the detrital (acid insoluble) metal concentration for some trace metals.

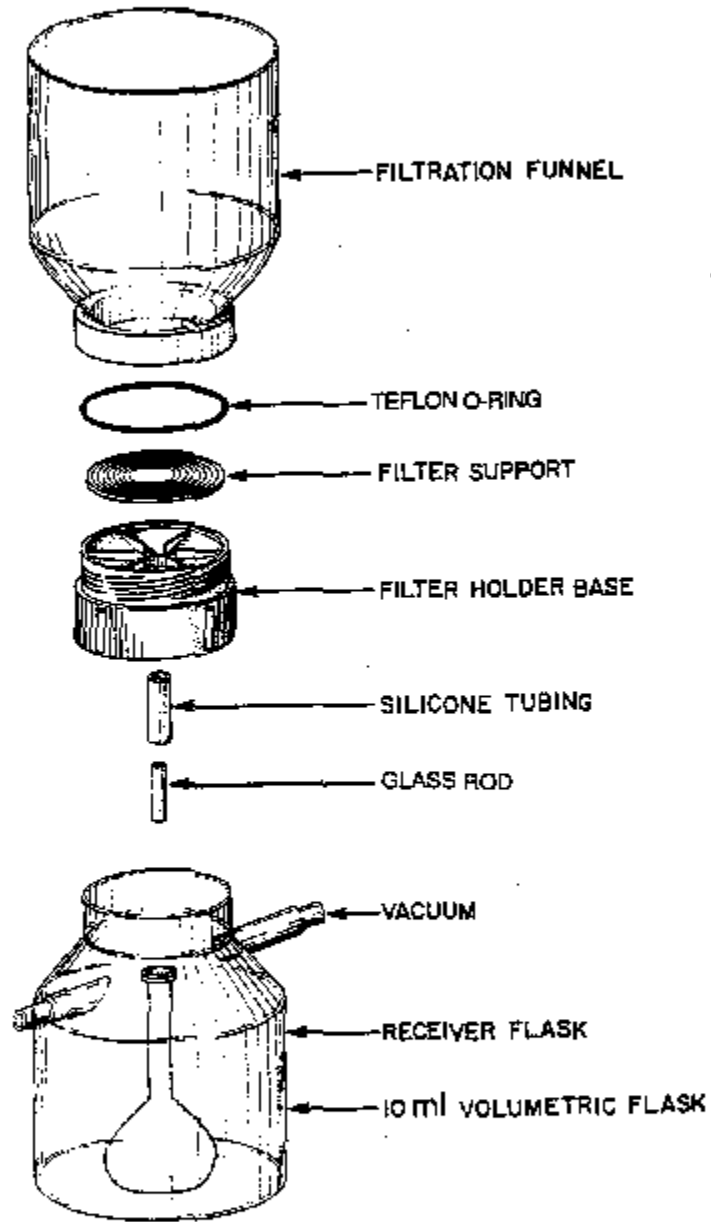


FIGURE 4: Apparatus for Acetic Acid Extraction of SPM (Loring and Rantala, 1990).

- (d) Coated L'vov platforms are used for Al and Ni determinations;
- (e) No platform is used for Cu which is determined using a pyrolytically coated tube.

14.14 L'vov platform conditioning for Cd

It was found that the platform had to be conditioned for the Cd determination in the acetic acid matrix to ensure reproducible results. Reproducible results can be obtained by running a conditioning solution made up of a HOAc sediment leachate (2g/50 ml) at the beginning of the analyses and between each sample and standard.

14.15 Furnace control program steps

The furnace controller programs used are shown in Table 4. In addition, two other steps are used.

- (a) The residual matrix is removed by a 3 sec firing at 2700°C and the platform should be cooled for 15 sec at 20°C before the next sample is introduced into the furnace;
- (b) It is also necessary to lower the atomization temperature for Cd from 1600°C in the H₃BO₃ matrix to 1100°C in the acetic acid matrix;
- (c) Internal argon flow is reduced to 50 ml/min during atomization. The gas interrupt mode is used for low levels of Cd.

14.16 Data reporting

SPM metal data may be reported on a dry weight or unit per volume basis or both. Unit per volume requires least work since the weighing of the filter is not necessary and only the volume of the water passing through the filter is measured. This method, however, also gives the least information.

The additional time to weigh the filters before and after SPM collection results in valuable data that otherwise would not be obtained. SPM concentration in the water column can now be calculated and metal concentrations expressed both on a dry weight and on a unit per volume basis.

This makes it possible to determine if the metal levels are due to the amount of SPM in the water column or due to the concentrations in the particles themselves. It also allows comparison with sediment trap and bottom sediment data.

14.17 Results of intercomparison exercise (s) for particulate metals

The data shown in Table 9 compares the values obtained from the determination of various particulate metals in samples used for intercomparison exercise using the procedures shown above. The results show that the values obtained by using proposed methodology compare well with those obtained by other laboratories.

15. GUIDELINES FOR THE NORMALIZATION OF GEOCHEMICAL DATA

15.1 Introduction

In many estuaries and coastal regions adjacent to industrial and urban high latitude areas of eastern North America ($>42^\circ$) and western Europe ($>52^\circ$), sediments are the largest repository and potential source of metallic contaminants in the marine environment.

Since metals from natural and anthropogenic sources accumulate together, it is difficult to determine what proportion of the sedimentary metal load is natural and what proportion is anthropogenic. This is because of variable anthropogenic inputs and natural sedimentary metal loads that can vary by several orders of magnitude, depending on the nature, grain size distribution and provenance of metal-rich/metal-poor minerals/compounds in the sediments.

In most areas, hydraulic and mineralogical (chemical) particulate fractionation usually results in increasing heavy metal concentrations with decreasing sedimentary grain sizes. It is essential, therefore, to understand, and normalize for, the effects of grain size distributions and provenance on natural metal variability, before the effects of anthropogenic metallic inputs can be assessed.

This section reviews various granulometric and geochemical approaches that can be used to determine background levels of heavy metals and to normalize for the grain size effects on natural metal variability in different samples so that anthropogenic metal contributions may be quantified. Its purpose is to demonstrate how to collect sufficient data to normalize for the grain size effect and to allow detection, at various levels, of anomalous metal concentrations within estuarine and coastal sediments. More information is given in UNEP/IAEA Reference Methods for Marine Pollution Studies No. 58 "Guidelines for the use of sediments for marine pollution monitoring programmes".

15.2 Requirements for geochemical data

For any study of sediments, a basic amount of information on their physical and chemical characteristics is required before an assessment can be made on the presence or absence of anomalous metal concentrations. The levels at which contamination can be detected depends on the sampling level and the number of physical and chemical variables that are determined for individual samples.

15.2.1 Field sampling

Briefly, repeated sampling of sediments is required to establish spatial and temporal trends in trace metal concentrations of a given area. A gridded sampling pattern is often used when sampling for spatial trends, but sometimes a pattern based on submarine morphology is necessary to ensure that representative samples of all sediment types are obtained. The high variability of the sediment characteristics requires the consideration of a sufficient number of samples. This number can be evaluated by an appropriate statistical analysis of the variance within and between samples.

In order to determine the total metal concentration, by atomic absorption spectrometry (AAS) (Section 9), or inductively coupled plasma atomic emission spectrometry (ICP), it is necessary to decompose the sediment sample in such a way as to release the metals from minerals and compounds with which they reside. The use of a reliable and repeatable decomposition technique (Section 7) involving HF + aqua regia has a decisive effect on the amount and quality of analytical data and is the basic condition for obtaining precise and accurate data (Loring and Rantala, 1988).

15.2.3 Selection of metals

The trace metals to be determined depend on the purpose of the investigation. Usually Hg and Cd are considered to be the most environmentally critical metals, followed by Pb. In addition, the concentrations of Zn and Cu are usually determined although they seldom reach levels in the sediments that are toxic to organisms.

For normalization purposes, determinations of at least Li and/or Al are also recommended followed by Fe and Mg in order to account for the metal variations in respect to the variations of the aluminosilicate mineral fraction. Determination of the carbonate and organic matter contents are also recommended because carbonate may be an important diluent (carrier under certain conditions) and organic matter is sometimes an important concentrator of trace metals, particularly Hg and Cd in the sediments.

15.3 Background levels

It is necessary to establish natural background metal levels before the extent, if any, of heavy metal contamination can be estimated. Such background levels are subtracted from the total values to yield an estimate of the anthropogenic contribution.

Background levels can be estimated by:

- (a) Average metal concentrations of texturally-equivalent sediments reported in the literature.
- (b) Direct measurements of metal concentrations in recent texturally and mineralogically-equivalent sediments from a known pristine region.
- (c) Direct measurements of metal concentrations in texturally-equivalent sub-surface core samples obtained from a depth below any possible contamination or biological mixing.

15.4 Normalization procedures

Simple to more complex approaches can be used to normalize geochemical data for the grain size effect and identify anomalous metal concentrations. The approach used depends on the requirements and resources of the investigation. Table 10 summarizes the role of various factors used for normalization of trace metal data.

- (a) Significant granular variations occur between sediment samples.
- (b) A strong significant relationship, at least at the 95% confidence level (the 99% level would be preferred), should exist between the metal content and the relevant parameter.
- (c) The regression line which expresses the significant relationship should ideally follow the Equation $y = ax$ instead of the form $y = ax + b$.
- (d) It should be possible to provide accurate and precise analysis of the metal and the relevant parameter to limit errors of measurements of x and y that may mask some of the natural variability of the parameters.

15.4.3 Metal : grain size normalization

One common procedure used to account for trace metal variability is the mathematical normalization to grain size. Application to trace metal data usually shows that decreasing grain size with increasing metal concentrations occurs consistently but the strength of the relationship depends on the metal and the sedimentary environment because of variations in mineralogical composition related to origin rather than particle size.

To establish the relationship between the metal and grain size, the concentrations of the metal are plotted, for example, against the percentage of the mud size fraction.

In most cases, some sort of linear relationship emerges of the general form $y = ax + b$, the strength of which is measured by the correlation coefficient (r). A linear relationship of the form $y = ax$ is uncommon because the sand size fractions usually contain some trace metals, the amount of which can be estimated from the intercept of the Y axis.

If the relationship is significant ($p \leq 0.05$ or 0.01), a regression line should be calculated and graphed along with a 95% or 99% prediction band so that the natural geochemical population of that metal in relation to grain size changes can be defined. This means that there is a 95% or 99% probability that the points which fall outside the prediction band are from a different or anomalous population.

For example, Figure 5 shows a linear plot that takes the form of $y = ax + b$ for Zn concentrations in relation to the mud (material $< 53 \mu\text{m}$ in diameter) content (percentage by weight) in sediments from the St. Lawrence estuary (Loring, 1978). It shows Zn varies significantly ($r=0.82$, $p<0.001$) with the mud content of the sediments. The proportional changes in Zn concentrations with changes in mud content within a narrow confidence band indicate that the data meet the criteria for mathematical metal-grain size normalization and allow for the compensation of the grain size effect on the natural Zn population.

TABLE 10
Summary of Normalization Factors

Normal Factor Textural	Size (μm)	Indicator	Role
Grain Size	2000-<2	Granular variations of metal bearing minerals/ compounds	Determines physical sorting and depositional pattern of metals
Sand	2000-63	Coarse grained metal-poor minerals/compounds	Usually diluent of trace metal concentrations
Mud	<63	Silt and clay size metal bearing minerals/ compounds	Usually overall concentrator of trace metals*
Clay	<2	Metal-rich clay minerals	Usually fine grained accumulator of trace metals*
Chemical			
Si		Amount and distribution of metal-poor quartz	Coarse grained diluter of trace metal concentrations.
Al		Al silicates, but used to account for granular variations of metal rich fine silt + clay size Al- silicates	Chemical tracer of Al- silicates, particularly the clay minerals*
Fe		Metal-rich silt + clay size Fe bearing clay minerals, Fe rich heavy minerals and hydrous Fe oxides	Chemical tracer for Fe-rich clay minerals.
Sc		Sc structurally combined in clay minerals	Tracer of clay minerals which are concentrators of trace metals
Cs		Cs structurally combined in clay minerals and feldspars	Tracer of clay minerals which are concentrators of trace metals
Li		Li structurally combined in clay minerals and micas	Tracer of clay minerals, particularly in sediments containing Al-silicates in all size fractions.
Organic Carbon		Fine grained organic matter	Sometimes accumulator of trace metals like Hg and Cd

* except in sediments derived from glacial erosion of igneous rocks

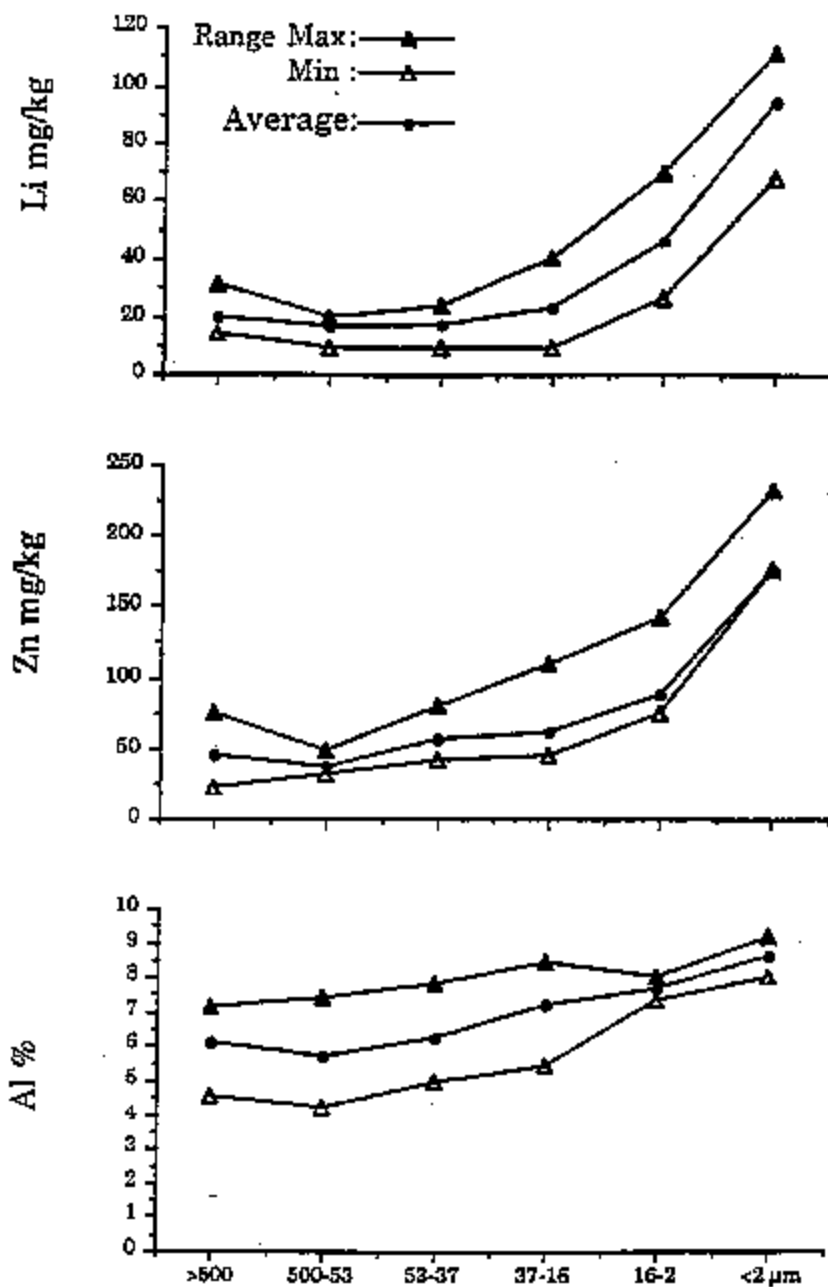


FIGURE 6: Changes of Li, Zn, and Al concentration with size in 13 samples from different parts of the Gulf of St. Lawrence. Data from Loring, 1978.

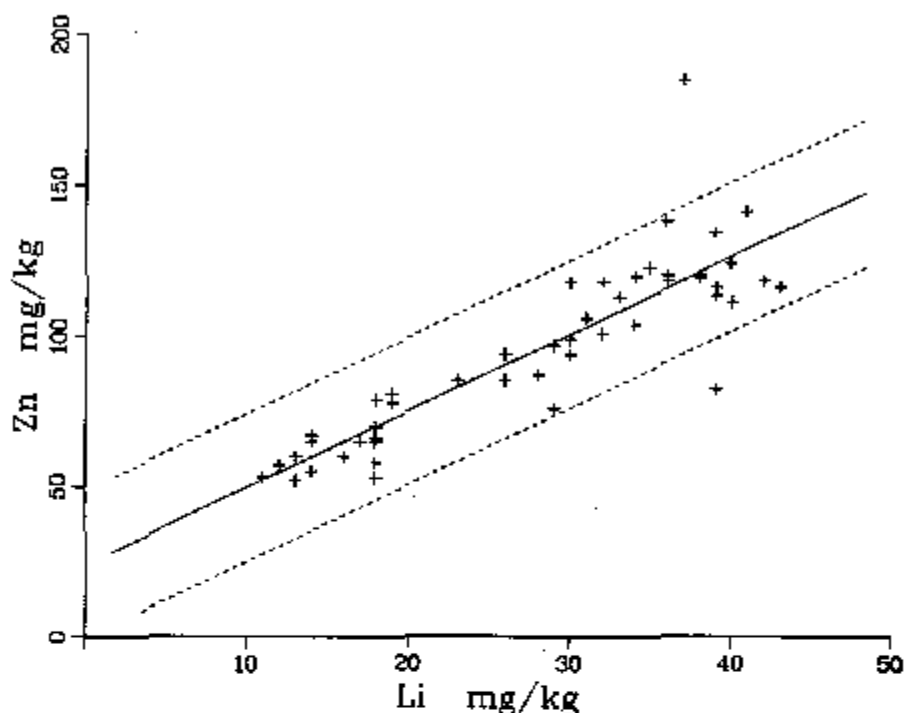


FIGURE 7: Zn: Li scatter plot for the St. Lawrence estuary ($n=49$; $r=0.87$). Solid line represents the regression line. Parallel dashed lines define the 95% confidence band. Data from Loring, 1978.

15.5 Multi-element normalization

A multi-element/component study in which the major and trace metals along with grain size and organic carbon contents have been measured allows the inter-relationships between the variables to be established in the form of a correlation matrix. From such a matrix, the most significant trace metal: relevant parameter(s) be it grain size, Al, Li, or organic carbon can be determined and used for normalization, identification of metal carriers, and detection of anomalous trace metal values. Factor analyses can sort all the variables into groups (factors) that are associations of highly correlated variables so that specific and/or nonspecific textural, mineralogical, and chemical factors controlling the trace metal variability may be inferred from the data set (Loring 1978, Spencer, 1968).

15.6 Summary of normalization procedures

The use of the granulometric measurements, metal/Al, metal/Li, or other element ratios are all useful approaches towards complete normalization of granular and mineralogical variations, and identification of anomalous metal concentrations in sediments. Their use requires that a large amount of good analytical data be collected and specific geochemical conditions be met before all the natural metal variability is accounted for, and the anomalous metal levels can be detected. Anomalous metal levels, however, may not always be attributed to contamination but rather could easily be a reflection of differences in sediment provenance.

These basic elements of quality assurance programmes define the framework which supports written protocols, and all laboratory procedures.

Reference materials are available from United Nations and national sources. These consist, among other items, of homogenized marine sediments which can be distributed to interested laboratories on a regular basis. These materials should be used by the laboratories to establish their precision and accuracy for the determination of trace elements in marine sediments by performing the initial analysis of three aliquots of the reference material. Levels should be tabulated on a dry weight basis. Means and standard deviations should be computed for each compound quantified. This data will establish the precision of replicate analysis for each result tabulated. Intercomparison with the results of other reputable laboratories will aid in the assessment of accuracy.

16.3 Analytical Quality Control Charts (AQCCs)

16.3.1 Purpose of AQCCs

It has been recommended that a reference material should be analysed periodically to provide a check on the quality of analytical data. The simplest way to assess the results of these analyses is to examine them at the end of the analytical period and decide whether or not they are satisfactory, and thus whether or not the results for samples are acceptable. This approach is very subjective and a much better approach is to plot the results of the analysis of RMs on a simple chart, which contains guidelines that allow an objective decision to be made on the quality of the data. This chart is known as an analytical quality control chart (AQCC).

16.3.2 Construction of an AQCC

Analysts are reminded that before a method is used routinely for samples it must have been rigorously assessed to ensure that it will provide data of the required quality. Assuming that such a method is used the analyst should carry out the following procedure to construct an AQCC, along the lines of that given below in Figure 8.

- (i) Select the RM to be analyzed with samples on a regular basis.
- (ii) Analyze the RM at least 10 times for the analyte(s) under examination. These analyses should not be done on the same day but spread out over a period of time in an attempt to ensure that the full range of random errors within and between batch analyses are covered.
- (iii) Calculate the mean value (\bar{X}), and the standard deviation (s) and then plot the following values on a blank control chart:

\bar{X} , $\bar{X}+2s$ (UWL), $\bar{X}+3s$ (UCL), $\bar{X}-2s$ (LWL) and $\bar{X}-3s$ (LCL).

- (d) If the result falls outside the UCL or LCL lines then the analyst should check the analytical procedure to determine the cause of this source of error.

If any of the above cases occur the analyst should reject the results of the analysis of the particular batch of samples and should not carry out any further analysis of samples until the source(s) of the errors have been identified and he/she is satisfied that future analyses will be under control.

16.3.4 Use of Internal Reference Materials

The accuracy of a method can only be checked with a CRM for which the mean values and standard deviations are well documented. Analysts who choose to use their own specially prepared RM (i.e., an Internal RM, IRM) for quality control purposes should note that they are primarily checking the precision of measurements and not their accuracy. These IRMs are very convenient, especially when the cost of CRMs for construction of QC charts would be prohibitive. Full instructions on the preparation and calibration of IRMs will be given in another publication in the present series.

16.4 Definitions of some relevant statistical terms

The **specificity** of an analytical chemical method is the degree to which the mean value of the measurements is due to the substance to be determined and not to other substances that may be present in the sample being analysed.

The **sensitivity** of an analytical chemical method is the smallest change in the quantity to be measured which produces a detectable change in the output. In this case it is synonymous with the term minimum detectability.

The **precision** of an analytical chemical method is the degree to which one representative determination of a substance in a sample will yield a measurement that approaches the average measurement of an infinite number of determinations of the same sample (in other words, the precision is the reproducibility of the analytical results).

The **accuracy** of an analytical chemical method is the degree to which the mean value of the measurements obtained by the method approaches the true value for the measured substance (the effects of other substances interfering being eliminated physically or mathematically).

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