REGIONAL SEAS

UNITED NATIONS ENVIRONMENT PROGRAMME FEBRUARY 1995

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

Reference Methods For Marine Pollution Studies No. 63

UNEP 1995

NOTE: This document has been prepared jointly by the Intergovernmental Oceanographic Commission (IOC), the International Atomic Energy Agency, Marine Environment Laboratory (IAEA-MEL) and the United Nations Environment Programme (UNEP) under the project FP/ME/5101-93-03(3033).

For bibliographic purposes this document may be cited as:

UNEP/IOC/IAEA: Manual for the geochemical analyses of marine sediments and suspended particulate matter. Reference Methods for Marine Pollution Studies No. 63, UNEP 1995.

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
IAEA Marine Environment Laboratory
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MC-98012 MONACO Cedex

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.

This Reference Method was designed to update and replace a series of existing UNEP/IAEA Reference Methods for the determination of single trace elements in sediments and suspended matter originally released in 1985. The present document is entirely based on a paper by Loring and Rantala (1) and edited according to the standard format for Reference Methods. Permission to reprint the article from the authors and Elsevier Science B.V., Amsterdam, The Netherlands, is gratefully acknowledged.

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(1) Loring, D.H. and Rantala, R.T.T. 1992. Manual for the geochemical analyses of marine sediments and suspended particulate matter. Earth-Science Reviews, 32: 235-283.

CONTENTS

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.

2. REFERENCES AND LITERATURE FOR CONSULTATION

American Chemical Society. 1980. Guidelines for data acquisition and data quality evaluation in environmental chemistry. *Anal. Chem.* 55: 2242-2249.

Bartlett, R. and James, B., 1980. Studying dried, stored soil samples-some pitfalls, *Soil. Sci. Am.*, 44: 721-724.

Bouma, A .H., 1969. Methods for the study of sedimentary structures, Robert E. Kreiger Publishing Co. Huntington, New York, 157pp.

Feldman, C., 1974. Preservation of dilute mercury solutions. *Anal. Chem.* 46: 99-102.

Flanagan, F.J., 1984. Three USGS mafic rock reference samples, W-2, DNC-1, and BIR-1. *U.S. Geol. Surv. Bull.*. 1623, 54 pp.

Gaudette, H.E., Flight, W.R., Toner, L., and Folger, D.W., 1974. An inexpensive titration method for the determination of organic carbon in recent sediments. *J. Sed. Pet.* 44: 249-253.

Gladney, E. and Roelandts, I., 1988 a. 1987 compilation of elemental concentration data for USGS BIR-1, DNC-1, and W-2. *Geostandards Newsl.* 12: 63-118.

Gladney, E. and Roelandts, I., 1988 b. 1987 compilation of elemental concentration data for USGS BHVO-1, MAG-1, QLO-1, RGM-1, SCO-1, SDC-1, SRG-1, and STM-1. *Geostandards Newsl.* 12: 253-362.

Govindaraju, K., 1989. 1989 Compilation of working values and sample description for 272 geostandards. *Geostandards Newsl.* 13, Special Issue. 113p.

Hatch, W.R., and Ott, W.L., 1968. Determination of sub-microgram quantities of mercury by atomic absorption spectrophotometry. *Anal. Chem.* 40: 2085-2087.

Hinderberger, E.J., Kaiser, M.L., and Koirtyohann, S.R., 1981. Furnace atomic absorption analysis of biological samples using the L'vov platform and matrix modification. *Atomic Spectrosc.* 2: 1-7.

IOC Manuals and Guides 25, Standard and Reference Materials for Marine Science. Revised edition, 1993.

Jackson, M.L., 1958. Soil chemical analysis. Prentice Hall, New York, NY. 485p.

Kersten, M., and Forstner, U., 1987. Effect of sample pretreatment on the reliability of solid speciation data of heavy metals-implications for the study of early diagenetic processes. *Mar. Chem.* 22 : 299-312.

Kingston, H.M., and Jassie, J.B., 1986. Microwave energy for acid decomposition at elevated temperatures and pressures using biological and botanical samples. *Anal. Chem.* 58: 2534-2541.

Kothandaraman, P., and Dallmeyer, J.F., 1976. Improved desiccator for mercury cold vapour technique. *At. Absorp. Newsl.* 15: 120-121.

Loring, D.H., 1975. Mercury in the sediments of the Gulf of St Lawrence. *Can. J. Earth Sci.* 12: 1219-1237.

Loring, D.H., 1978. Geochemistry of zinc, copper, and lead in the sediments of the estuary and Gulf of St Lawrence. *Can. J. Earth Sci.* 15: 757-772.

Loring, D.H., 1981. Potential bioavailability of metals in eastern Canadian estuarine and coastal sediments. *Rapp. P.v. Reun. Cons. int. Explor. Mer.* 181: 93-101.

Loring, D.H., 1987. A final report on the ICES intercalibration for trace metals in marine sediments (1/TM/MS). *Int. Explor. Mer.* (Copenhagen, DK). 143: 134pp.

Loring, D.H., 1990. Lithium - a new approach for the granulometric normalization of trace metal data. *Mar .Chem.* 29: 155-168.

Loring, D.H, and Asmund, G., 1989. Heavy metal contamination of a Greenland fjord system by mine wastes. *Environ. Geol. Water. Sci.* 14: 61-71.

Loring, D.H., and Nota, D.J.G., 1973. Morphology and sediments of the Gulf of St Lawrence. *Fish. Res. Bd. Can. Bull.* 182: 147pp.

Loring, D.H. and Rantala, R.T.T., 1988. An intercalibration exercise for trace metals in marine sediments. *Mar.Chem.* 24: 13-28.

Loring, D.H. and Rantala, R.T.T., 1988. An intercalibration exercise for trace metals in marine sediments. *Mar.Chem.* 24: 13-28.

Loring, D.H. and Rantala, R.T.T., 1990. Sediments and suspended particulate matter: Total and partial methods of digestion. *ICES Tech. Mar. Environ. Sci. 9 int. Explor. Mer* (Copenhagen, DK) 14pp.

Loring, D.H., Rantala, R.T.T. 1992. Manual for the geochemical analyses of marine sediments and suspended particulate matter, *Earth-Science Reviews*. 32: 235-283.

Loring, D.H., Rantala, R.T.T., Morris, A.W., Blake, A.J., and Howland, R.J.M., 1983. Chemical composition of suspended particles in an estuarine turbidity maximum zone. *Can. J. Fish. Aqu. Sci.*, 40, Supp. No 1: 201-206.

Loring, D.H., Rantala, R.T.T. Morris, A.W., and Asmund G., 1985. Non-detrital and detrital particulate metal transport in estuarine systems. In: Planetary Ecology, D.E.Caldwell, J.A. Brierley, C.L. Brierley (eds). Van Nostrand Reinhold Company, N.Y.: 187-197.

Luoma, S.N.,and Jenne, E.A. 1976. Estimating bioavailability of sediment-bound trace metals with chemical extractants. In: Trace Substances in Environmental Health, D.D. Hemphill (Ed.). Univ. of Missouri Press, Columbia, MO.: 343-351.

Muller, G., 1979. Schwermetalle in den sedimenten des Rheims-Veranderungen seit. *Umschau* 79: 778-783.

Nirel, P.V.M., and Morel, F.M.M., 1990. Pitfalls of sequential extractions. *Wat. Res.* 24: 1055-1056.

Rantala, R.T.T., and Loring, D.H., 1977. A rapid determination of 10 elements in marine suspended particulate matter by atomic absorption spectrophotometry. *At. Abs.* Newsl. 16: 51-52.

Rantala, R.T.T. and Loring, D.H., 1978. Atomic absorption analysis of USGS reference sample: Marine Mud MAG-1 for selected trace elements. *Geostandards Newsl.* 2: 125-127.

Rantala, R.T.T., and Loring, D.H., 1980. Direct determination of cadmium in silicates from a fluoboric-boric acid matrix by graphite furnace atomic absorption spectrometry. *Atomic Spectrosc.* 1: 163-165.

Rantala, R.T.T., and Loring, D.H., 1985. Partition and determination of cadmium, copper, lead and zinc in marine suspended particulate matter. *Intern. J. Environ. Anal. Chem.* 19: 165- 173.

Rantala, R.T.T., and Loring, D.H., 1987. Cadmium in marine sediments: Determination by graphite furnace atomic absorption spectroscopy., *ICES Tech. Mar. Environ. Sci.* 3 *int. Explor. Mer* (Copenhagen, DK) 9pp.

Rantala, R.T.T., and Loring, D.H., 1989. Teflon bomb decomposition of silicate materials in a microwave oven. *Anal. Chim. Acta.* 220: 263-267.

Rantala, R.T.T., and Loring, D.H., 1990. Determination of Lithium in NRCC sediments: MESS-1, BCSS-1, PACS-1 and the NIST river sediment: SRM 2704. *Geostandards Newsl.* 14: 475-476.

Slavin, W., 1988. Graphite furnace AAS for biological materials. *Sci. Tot. Environ.* 71: 17-35.

Spencer, D.W., Degens, E.T., and Kulbicki, G., 1968. Factors affecting element distribution in sediments. In: Symposium on the Origin and Distribution of the Elements, L.H. Arhens (ed.). Pergamon Press, New York: 981-999.

Sturgeon, R.E., Desaulniers, J.A., Berman S.S., and Russell, D.S., 1982. Determination of trace metals in estuarine sediments by graphite furnace atomic absorption spectrometry. *Anal. Chim. Acta.* 134: 283-291.

Tanner, C.B., and Jackson, M.L., 1947. Nomographs of sedimentation times for soil particles under gravity of centrifugal acceleration. *Soil Sci. Soc. Proc.*: 60-65.

Tessier, A., Campbell, G.C., and Bisson. M., 1979. Sequential extraction procedure for the speciation of particulate trace metals. *Anal. Chem.* 51: 844-851.

Thompson, K.C., 1978. Shape of the atomic-absorption calibration graphs for chromium using an air-acetylene flame. *Analyst.* 103: 1258-1262.

Thompson, E.A., Luoma, S.N., Cain, D.J., and Johansson, C., 1980. The effect of sample storage on the extraction of Cu, Zn, Fe, Mn and organic material from oxidized estuarine sediments. *Water, Air, and Soil Pollut.* 14: 215-233.

Tyson, J.F., 1984. A critical look at calibration procedures for flame atomic absorption spectrometry. *Analyst.* 109: 313- 317.

UNEP/IOC/IAEA/FAO. Contaminant monitoring programme using marine organisms: Quality Assurance and Good Laboratory Practice. Reference Method for Marine Pollution Studies No.57. UNEP 1990.

Veillon, C., 1986. Trace element analysis of biological samples. *Anal. Chem.* 58: 851A-866A.

Walkey, A., 1947. A critical examination of a rapid method for determining organic carbon in soil. *Soil Sci.* 63: 251-263.

Windom, H.L., 1987. Guide to the interpretation of reported metal concentrations in estuarine sediments. Florida Dept. of Environ. Regulation (Tallahassee, Florida) 43pp.

Windom, H.L., Schropp, S.J., Calder, F.D., Ryan, J.D., Smith, Jr.R.G., Burney, L.C., Lewis, F.G., and Rawlinson, C.H., 1989. Natural Trace metal concentrations in estuarine and coastal marine sediments of the southeastern United States. *Environ. Sci. Technol.* 23: 314-320.

Yeats, P.A., and Brugmann, L., 1990. Suspended particulate matter: Collection methods for gravimetric and trace metal analyses. *ICES Tech. Mar. Environ. Sci. 7 Int. Explor. Mer* (Copenhagen, DK) 9 p.

Yeats, P.A. and Dalziel, J.A., 1987. ICES intercalibration for metals in suspended particulate matter. *J. Cons. int. Explor. Mer.* 43: 272-278.

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.

Organic carbon is often determined to assess the role played by the organic fraction of sediments in the transport, deposition and retention of metals in sediments. Section 12 details the Walkey-Black titration procedure used in our laboratory for the determination of readily oxidizable organic matter using cold sulfuric acid and potassium dichromate.

Carbonate is sometimes an important component of sediments. Section 13 details a simple method for the estimation of carbonate contents of sediments.

Suspended particulate matter (SPM) is often the conduit by which heavy metals are carried, removed, and deposited in the marine environment. Section 14 details the procedures used for the sampling and preparation of SPM for metal analyses. Detailed instructions are found in this section for the decomposition of SPM samples with HF and aqua regia in sealed teflon vessels, the extraction of loosely bound metals with acetic acid, and the atomic absorption techniques used for the determination of the metals.

Since metals from natural and anthropogenic sources accumulate together, it is difficult to distinguish between the proportions of the sedimentary metal load that are respectively natural and anthropogenic. This is because of anthropogenic and natural metal inputs that vary by several orders of magnitude, depending on the nature, grain size, and source of the metal rich / metal poor minerals or compounds in the sediments. The final part of the manual (Section 15) presents sampling, analytical, and interpretative guidelines for the normalization of geochemical data to account for the natural sedimentary variability. These guidelines are essential for evaluating the extent, if any, of metal contamination of marine sediments.

4. SAMPLING ESTUARINE AND COASTAL SEDIMENTS

4.1. Estuarine sediment classification

Estuarine and coastal sediments may be regarded as a mixture of inorganic and organic material that has arrived at the site of deposition as solid particulate matter (detritus) or has been incorporated into the sediments from solution (non-detrital) in a variety of ways. They may be classified according to their grain size and relative proportion of the sediment particles, their color, the relative proportion of their organic and inorganic components, and their predominant chemical (siliceous, calcareous), and mineralogical composition. In most northern latitude sediments, detrital material dominates the non-detrital material and determines the broad chemical composition of the sediments. The organic component of such sediments is normally less than 10% by weight.

4.2 Sample collection and field observations

Samples of marine sediments and suspended particulate matter may be collected from the sea floor and from the water column using specific types of sampling apparatus. This is done to ensure that the sample is fully representative of the substrate or water column at a specific geographical location and that it is uncontaminated by any substance that is being analyzed for or that will interfere with the subsequent treatment of the sample.

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

sample should be frozen quickly for return to the laboratory. Larger samples of about 1 kg are required for admixtures of gravel, sand and mud.

4.2.2 Barrel core sub-surface sediment sampling

Sediment subsurface samples are often taken using barrel or box corers to determine the change in lithology and chemical composition with depth in order to assess environmental changes in metal fluxes with time. Cores are usually collected in areas of fine-grained sediments but specialized corers are available for coarse-grained sediments.

The main types of corers having cylindrical barrels are: a) the gravity corer which free-falls from the ship and penetrates the sea floor by gravity, and b) the piston corer which is released a set distance above the sea floor, penetrates the sediment by free fall, and sucks the sediment into the core barrel by an upward moving piston as the core is retrieved.

Plastic core liners are placed inside the core barrels to contain the sediment core sample and to avoid the problems of extrusion and contamination that occur in unlined barrels. In general, the greater the diameter of the liner, the less will be the amount of distortion of the subsurface sediment by the corer penetrating the sediments. Core liners with internal diameters > 50mm are usually satisfactory for obtaining samples for geochemical purposes.

After the corer is retrieved, the liners are capped at the bottom; the liner is removed from the barrel; the top is capped, and the core stored in a vertical position until all the water inside the liner has risen to the top. The liner is cut off at the sediment - water interface, capped and placed in a deep freezer or a cold room (4°C) for transport to the laboratory. Visual observations and measurements of sediment core samples should include information on the site number and location, depth, time, core length, lithology, stratigraphy, and any distortions in sediment layers.

In the laboratory, core sampling is best carried out by extruding the core upwards and slicing off layers (~ 1 cm) using a non-contaminating cutter (e.g. stainless steel, plexiglass) or splitting the plastic core liners lengthwise, avoiding the smeared zone around the inside of the core liners and sampling the interior section of the core. The samples are placed in containers for transport to the laboratory; plastic bags or wide-mouth jars (polypropylene or borosilicate glass) should be used for temporary storage. Prior to their use, containers and glass or plastic parts associated with the sampling equipment should be cleaned with detergent and then rinsed with metal-free water. The samples should be stored frozen, or at a sufficiently low temperature (~ 4°C) to limit biological and chemical activity. It is recommended that a minimum sub-sample size be 50 grams.

4.2.3 Box core sediment sampling

Rectangular sampling devices which obtain cores about 15-25 cm square and 15-60 cm deep are known as box corers and can be recommended for detailed sampling at or below the sediment-water interface. The advantage of the various types of box or square corers (Bouma, 1969) is that they can recover the surface sediment and fauna virtually intact. They can be subsampled by inserting several 5 cm diameter tubes into them. When sub sampling, however, the core material should be taken from the mid-part of the core to avoid any "edge effects". Such samples are treated in the same way as the core samples described above.

5. SAMPLE PREPARATION PROCEDURES

Figure 1 illustrates schematically the laboratory sequence for the determination of various physical and chemical parameters for marine sediments.

5.1 Sample preparation

Sample preparation for sedimentological and chemical analyses involves procedures for subsampling, drying, measurement of water content, wet and dry sieving, crushing and storage.

5.1.1 Laboratory equipment

Agate mortar and pestle.
Mechanical shaker.
Drying oven (drying ovens having teflon coated surfaces and a filtered nitrogen atmosphere are sometimes used to ensure against sample contamination).
Nylon or stainless steel sieves (2000, 500, 63, 37 μm diameter).
Atterburg Cylinders.
Evaporating dishes.
Analytical balance sensitive to 0.1 to 0.5 per cent of the sample weight.
Centrifuge: A large capacity centrifuge is highly desirable, although not absolutely necessary, for washing samples free of sea salts and for separating clay size fractions. The same centrifuge with a smaller head, or a centrifuge of smaller capacity, is also needed for separating the acetic acid soluble fraction.
Polypropylene or glass centrifuge bottles.

5.1.2 Initial preparation

The selection of subsamples for sedimentological and chemical analyses involves procedures for subsampling, drying, water content determination, and removal of the sea salts.

Extreme care must be taken during sample preparation, as always, to avoid metallic contamination by metallic objects, undecontaminated plastic and glassware and uncovered hands.

Initially, samples designated for chemical analyses of the total sediment are unfrozen and homogenized while still wet. The samples are dried, crushed lightly and subsamples removed for archiving, and for grain size separations. The coarse material >2mm such as pebbles, coarse organic fibers and shells are removed by hand. The remaining material is again homogenized before being split into subsamples for the various chemical analyses by splitting and quartering. Representative samples are then obtained using plastic utensils.

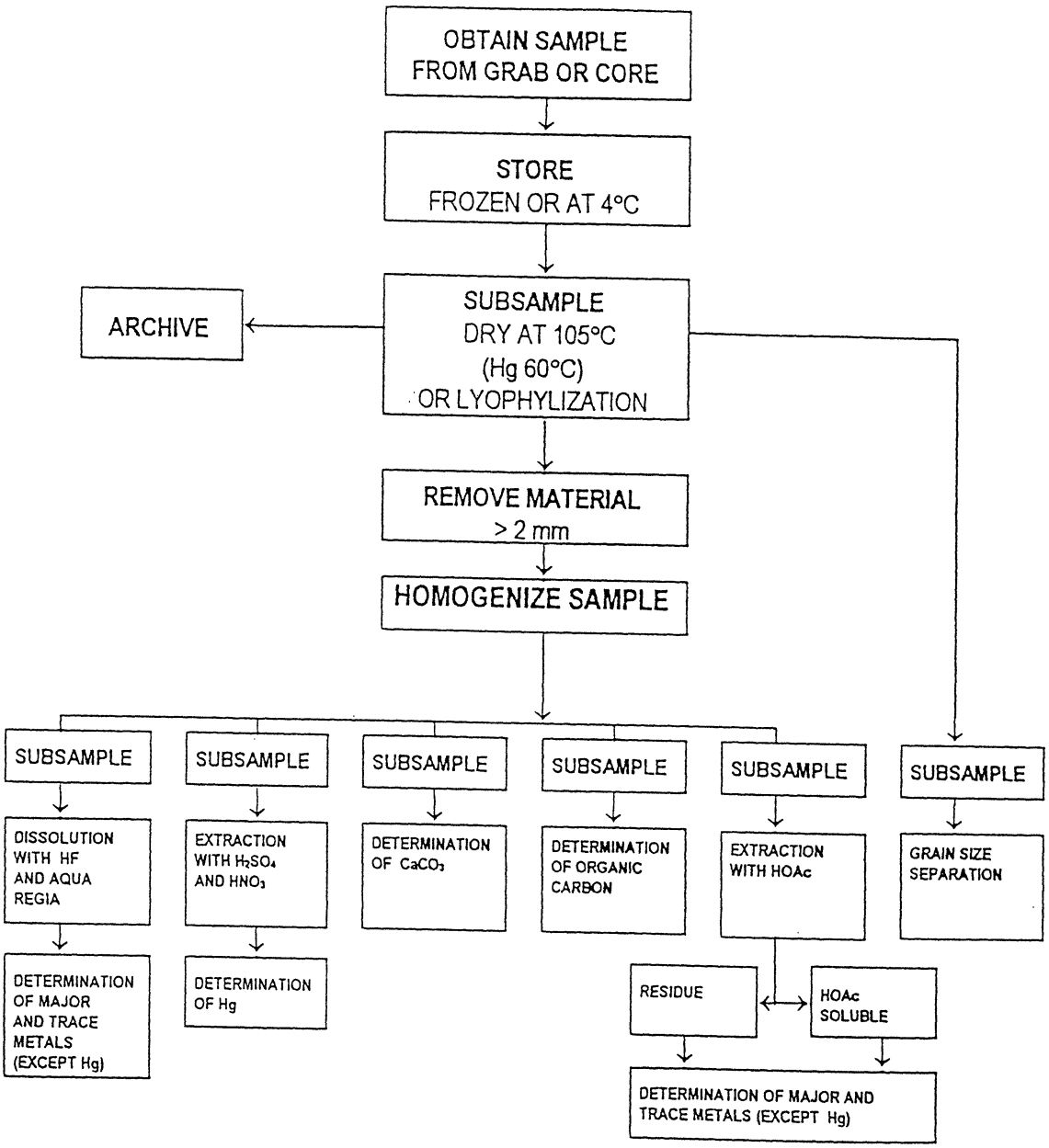


FIGURE 1: Sample Preparation and Analytical Sequence for Determinations of Physical and Chemical Parameters in Marine Sediments.

5.1.3 Drying sediments

Sediment samples must be dried before grain size and chemical analyses are conducted because analytical measurements are based on a constant dry weight.

(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 lyophylization) 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;

(c) After drying, place the samples in a desiccator until cool;

(d) When the samples reach room temperature, reweigh them (y grams);

(e) Calculate the water content (expressed in percentages) from the equation: water content % = weight loss [(x - y)/ x]100.

5.1.6 Determination of water content in air dried samples (Oven drying)

All the results should be expressed on an oven dry weight basis so that the results are independent of variations in air humidity.

(a) Follow the procedure outlined for wet samples (Section 5.1.5);

(b) When using an air dried portion of the sample, subtract percent air dry moisture found from the air dry sample weight to obtain the oven dry weight;

(c) Correction to obtain oven dry weight:

Weight of air dry sample = X grams
Air dry moisture content =A%
Oven dry Wt of samples = X- [(A/100) X].

5.1.7 Salt content correction

Corrections for salt content are required for samples containing large amounts (>70%) of interstitial salt water because high salt contents introduce significant errors in metal determinations. In many cases, an average salinity (35 ‰) and a density of 1.025 $g.cm^{-3}$ may be assumed for pore water but for sediments with a high water content (>90%), the pore water should be squeezed out and its salinity determined.

The corrections for salt content are made from the data obtained from the determination of the water content of wet samples (Section 5.1.5).

Calculate the salt correction from the following equation:

Weight (wt.) of sample wet = x grams
Wt. of sample dry = y grams
(x-y) = wt of water = (wt. of sea-water - wt. of salt)
Wt. of water + salt (g) = (X-Y)/1 x 1.025 (density of pore water)
X - 1.025(X-Y) = Wt. of dry mud (salt corrected).

5.1.8 Removal of soluble sea salts

In addition to correcting for the salt content of sediments containing high water contents, it is sometimes necessary to remove the soluble sea salts from the sediments before analyses. Removal of soluble sea salts is required for samples which are used for the determination of the major cations Na, K, which are also present in sea-water. This is done to

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 (>63μm) and mud (<63 μm) size material in the sediment sample;

(b) Place the sample in distilled or deionized water until it can be dispersed;

(c) Wet sieve the sample through a 63 μm sieve, brushing carefully to prevent particles from aggregating or sticking to it;

(d) Carefully remove the fraction retained on the sieve, and transfer it to a pre-weighed teflon evaporating dish;

(e) Dry it in the oven at 105°C, cool in a desiccator, and reweigh;

(f) Calculate the sand content (expressed in percentages) from the equation: sand content % = Wt. of sand fraction / wt of sample X 100;

(g) Retain the sand size material for detailed size analysis of this fraction;

(h) Collect the mud size material washed through the sieve, if required for further analysis, in a metal-free container;

(i) Concentrate the mud size material either by centrifuging, or by allowing time for settling;

(j) Decant excess water and dry* in an oven or freeze dry.

*Oven dried fine material tends to be very cohesive so freeze drying may be preferable. If finer fractions such as the amount of clay size fraction are to be determined (see below), the pipette method or settling cylinders are used with chemical dispersants to prevent aggregation. If, the absolute chemical compositions of separated subfractions are required, the dispersants must be non-contaminating such as a weak solution of metal-free ammonium hydroxide (NH_4OH).

Alternatively, for samples designated for the analyses of trace metals in separate size fractions, the bulk sample can be unfrozen and the sample wet sieved though a 63μm nylon or stainless steel sieve. A separate determination of water content is required to calculate the amounts of the sand and mud size material in the sample.

6.1.2 Detailed grain size separations for trace metal determinations

(a) Remove water soluble sea salts from 10-20 g of sample as described in section 5.1.8, but do not dry (This step is not required for trace metal determinations, but is only necessary if the major cations Na, K, Mg, and Ca are to be determined);

(b) Wet sieve salt free sample through a set of 500μm, 63μm, and 37μm stainless steel or nylon sieves, brushing carefully to prevent particles from aggregating or sticking to them;

(c) Collect the fractions from each sieve;

(d) Carefully remove the fraction retained on each sieve, and transfer it to a pre-weighed teflon evaporating dish;

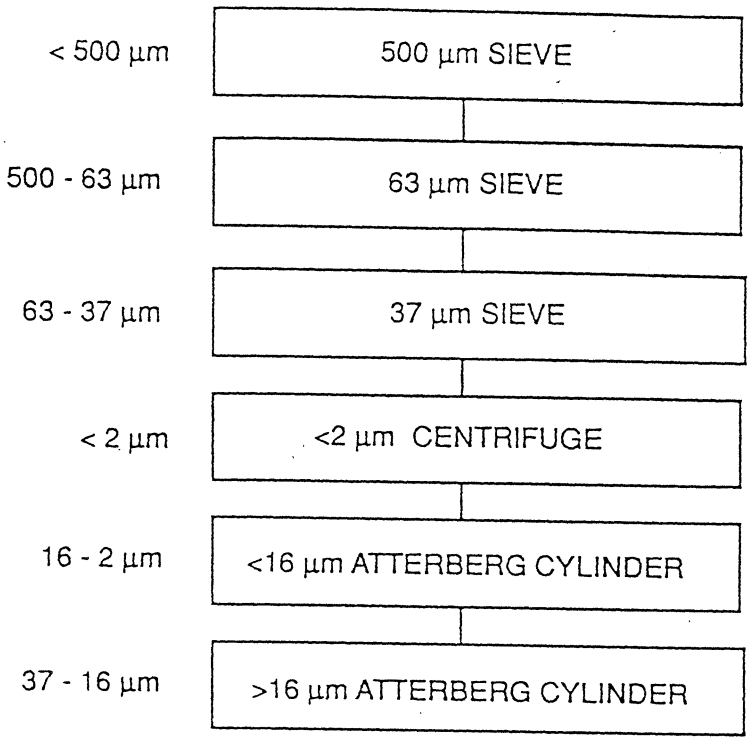


FIGURE 2: General Scheme for Grain Size Separation.

(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 NH_4OH as the dispersive agent;

(j) Shake mechanically for 30 minutes (an ultrasonic probe could be used instead of NH_4OH 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;

(m) Add 0.16N NH_4OH again, shake the centrifuge bottle mechanically, and centrifuge;

(n) Repeat the whole process until the supernatant siphoned off is clear. Usually four times is sufficient, although this depends on the amount of clay present;

(o) Centrifuge the stored <2μm fraction again to remove excess water;

(p) Transfer it to a pre-weighed teflon dish, dry at 105°C (60°C for Hg), cool in a desiccator, and weigh;

(q) Transfer the 37-2μm fraction from the bottle into an Atterberg cylinder, marked 30 cm from the bottom of the siphon tube;

(r) Make up to the mark with 0.16N NH_4OH, shake, and let stand for the specified time intervals shown in Table 1;

(s) Unclamp the siphon tube, and collect the 2-16μm fraction in the centrifuge bottle;

(t) Repeat until clear;

(u) Centrifuge off the excess water from the 2-16μm fraction;

(v) Transfer the fraction to a pre-weighed evaporation dish, dry at 105°C, cool in a desiccator and weigh;

(w) Transfer the 16-37μm fraction remaining in the Atterberg cylinder to a pre-weighed evaporation dish, dry at 105°C, store in a desiccator until cool, and weigh.

6.1.3 Storage of samples

Dried fractions are crushed, mixed, and stored in vials until required for analyses.

TABLE 1
Sampling Times for Size Fractions in Beaker or Atterberg Cylinder

Size Temp °C	<2μm 5 cm*	<4μm 5 cm	<8μm 10 cm	<8μm 30 cm	<16μm 30 cm
10	5 h 12'	1 h 18'	39' 0"	1h 57'	29' 15"
11	5 3	1 16	37 55	1 54	28 27
12	4 55	1 14	36 53	1 51	27 41
13	4 47	1 12	35 54	1 48	26 56
14	4 40	1 10	34 58	1 45	26 13
15	4 32.5	1 8	34 4	1 42	25 32
16	4 25.5	1 6.5	33 12	1 39	24 53
17	4 19	1 5	32 21	1 37	24 15
18	4 12	1 3	31 32	1 34	23 39
19	4 6	1 1.5	30 45	1 32	23 4
20	4 0	1 0	30 0	1 30	22 30
21	3 54	58.5	29 16	1 28	21 57
22	3 49	57	28 31	1 25	21 24
23	3 44	55.5	27 46		20 51
24	3 39	54	27 01		20 18

h hours;
' minutes;
" seconds
* Column from which particles larger than indicated have settled down in a specified time and temperature

7. GEOCHEMICAL ANALYSES OF SEDIMENTS

Geochemical analyses of sediments involves procedures for their decomposition and chemical analyses such as are outlined in Fig. 1. The number of steps that are followed will depend on the nature and extent of the investigation. It is recommended that, at least, the amount of material <63μm and the total trace concentrations be determined for each sample.

7.1 Sediment decomposition methods

In order to determine the major and trace metal concentrations of marine sediments by wet chemical methods, it is necessary to dissolve all or part of the sample. Sample digestion methods commonly used are: (a) Total decomposition; (b) Strong acid digestion, or (c) Moderate or weak acid extractions.

7.1.1 Total decomposition methods

Total decomposition methods use hydrofluoric acid (HF) in combinations with concentrated oxidizing acids such as aqua regia. Alternatively, alkaline fusion followed by acid dissolution of the flux can be used.

Hydrofluoric acid decomposition has the following advantages:

(a) HF is the only acid that completely dissolves the silicate lattices and releases all the associated metals such as Al, Fe, and Li used for the grain size normalization of the data.

(b) Accuracy can be assessed by analyzing reference materials certified for the total metal content.

(c) Intercomparable data, free from operationally defined bias, can be obtained.

Some laboratories have been reluctant to use HF due to its corrosive nature . After 30 years use, it is generally accepted that HF poses no greater danger than other strong acids 2when normal laboratory safety rules for handling acids are observed.

7.1.2 Strong acid (non-HF) digestion

Strong acid digestions using nitric acid (HNO_3) or aqua regia (HNO_3 + HCl) are commonly used to decompose marine sediments. They are NOT recommended for the following reasons:

(a) Strong acid digestions without HF result in incomplete digestions because silicates and other refractory oxides are not dissolved.

(b) The proportion of metals dissolved is variable and depends on the sample type, matrix, and element.

(c) Accuracy of the results can not be determined since no reference materials are certified for strong acid digestions.

(d) Metal data obtained from strong acid digestions are not intercomparable with total metal data and are subject to operationally defined bias.

7.1.3 Moderate or weak acid extractions

Moderate or weak acid extractions such as hydrochloric acid (HCl) and acetic acid (HOAc) are often used for chemical partition studies (Loring, 1978, 1981). They are strictly operationally defined procedures. Accordingly, they cannot be standardized using reference materials. The acetic acid (HOAc 25% v/v) extraction procedure is described in section 10 (marine sediments) and section 14 (suspended particulate matter).

8. TOTAL (HF) DECOMPOSITION OF SEDIMENTS

In this method (Loring and Rantala, 1990, Rantala and Loring, 1989), hydrofluoric acid and aqua regia are used to release the total metal content from marine sediments into solution in a sealed teflon decomposition vessel referred to as a teflon bomb. The teflon bomb decomposition procedure is shown in detail in a video available from International Counsel

for the Exploration of the Sea (ICES), Copenhagen, DK. It is also the method recommended for the ICES intercalibration exercise on trace metals in sediments (Loring, 1987).
The main advantages of the teflon bomb decomposition are:

(a) Rapid decomposition.

(b) Reduced risk of contamination.

(c) Small volume of acid required.

(d) No loss of volatile elements.

8.1 Apparatus and reagents

Teflon decomposition vessels (bombs), apparatus to heat the bombs, a mechanical shaker, and assorted plastic ware are the main items of equipment required to carry out the decomposition procedure.

8.1.1 Teflon bomb construction

The construction of the bomb must be such that no metallic contamination will occur; such risk is always present when steel clad bombs are used. LORRAN all teflon TFE decomposition vessels (Lorran International, Porters Lake, N.S., Canada, BOJ 2S0) of 20 ml capacity are used by the authors. These bombs can be submerged in boiling water and also heated in a microwave oven. The bombs incorporate a pressure relief mechanism for safety.

8.1.2 Teflon bomb heating equipment

The teflon bomb in which the sediment sample is decomposed is heated either in boiling water, or, in a more recent development, in a microwave oven to provide the necessary heat and pressure for the total decomposition of the sample.

(a) For heating the bomb by submersion in boiling water:
Hot plate.
Covered ceramic dishes (25cm x 25cm x 10cm deep). Each dish can accommodate 8 bombs at a time.
Sufficient water to cover the teflon bombs is placed into the ceramic dishes and heated to boiling on the hot plate.

(b) For microwave heating:
Microwave pressure cooker to contain any possible leakage of acid fumes.
Each cooker will accommodate 4 bombs at a time.
Flat based microwave safe dish to compensate for the concave bottom of the cooker.
Beaker, 100 ml.
Microwave oven with turntable.

The microwave oven should be calibrated to detect any decrease in the power output in the future and to facilitate the calculation of the optimum heating time for samples. The

temperature was found to be 20.9°C for the microwave oven Panasonic Model NE-7970C with 700W full capacity.

In microwave heating, some of the energy may be reflected back to the magnetron. As the magnetron heats the output decreases. To maintain reproducible conditions, the magnetron should be allowed to cool between sample heating periods.

The heating time depends on the power output of the microwave oven and the load. The optimum heating time can be estimated (Kingston and Jassie, 1986) and verified experimentally by analyzing certified reference materials and comparing the results to those obtained by a 1 hour decomposition in boiling water. Teflon bombs without pressure relief should not be used for microwave heating due to the potential danger of over-pressurization and explosion.

8.1.3 Laboratory equipment

Mechanical shaker.
Analytical balance.
Agate mortar and pestle.

8.1.4 Labware

Polypropylene volumetric flasks, 100 ml.
Polypropylene narrow mouth bottles.
Polystyrene disposable weighing boats.
Polypropylene graduated cylinders.
Polypropylene funnel.

No glassware should be used in the presence of HF as contamination might be released from the glass.

All labware should be thoroughly cleaned by soaking in dilute nitric acid and rinsing with de-ionized water.

Although the corrosive nature of HF is diminished when complexed with boric acid (H_3BO_3), the above precautions should be observed.

8.1.5 Reagents

Hydrofluoric acid [HF] (49%).
Nitric acid [HNO_3] (70%).
Hydrochloric acid [HCl] (37%).
Aqua Regia [HNO_3 - HCl] (1:3 v/v).
Boric acid crystals [H_3BO_3].
De-ionized reverse osmosis water.

All reagents must meet ACS analytical reagent grade requirements.

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 v/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;

(k) Rinse the bomb several times with deionized water and add the rinsings to the flask;

(l) Shake the flask to complete the dissolution (black carbon residue may remain but does not contain significant amounts of metals and does not interfere with subsequent metal determinations);

(m) Make the solution up to 100 ml with H_2O;

(n) Transfer the solution into a polypropylene bottle for storage;

(o) Allow solutions obtained from 100-500 mg sample size to settle overnight; those from 500-1000 mg sample size should settle for several days in case borosilicate forms. This is because the metals cannot be determined in concentrated solutions (> 500 mg sample/100 ml) until the gelatinous precipitate of borosilicates has settled, leaving a clear surface layer that can be analyzed. This process may take 7-14 days. When a smaller sample is used (<500 mg sample/100 ml), such precipitation will not occur and the sample may be analyzed after the black carbon residue has settled overnight;

(p) Analyze the solutions for trace metals by flame or graphite furnace AAS.

8.2.1 Storage of sample solutions

Store sample solutions in precleaned polypropylene bottles. Stored samples are 2extremely stable and it has been possible to determine Cd, for example, accurately in a clear surface layer after several years of storage.

9. ATOMIC ABSORPTION ANALYSES OF SEDIMENTS

Precise and accurate atomic absorption analyses for the determination of metals involves the use of flame (FAAS) and graphite furnace atomic absorption spectrophotometry (GFAAS).

FAAS is the method of choice for most metal determinations when the metals are present in sufficient concentrations to allow precise and accurate determinations.

GFAAS is generally used for the determinations beyond the sensitivity of FAAS. Due to improved accuracy and precision, GFAAS should be used for all Cd, Cr and Ni determinations. Pb should be determined by FAAS when concentrations are high enough; otherwise GFAAS should be used.

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 µl.
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 µg/ml standards. The 1000 µg/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.

9.2.1. Al, Ca, Fe, K, Mg, and Na multi-element standards

Prepare a combined stock standard solution of 300 µg/ml Al, and 100 µg/ml Ca, Fe, K, Mg, and Na from the 1000 µg/ml stock solutions by:

(a) Pipetting 30 ml of the Al stock solution, and 10 ml each of the Ca, Fe, K, Mg, and Na stock solutions into a 100 ml volumetric flask;

(b) Diluting the combined solution to 100 ml with de- ionized water.

Further dilute the combined stock solution 25, 50, 100, 200, and 400 times to prepare the working standards. All working standards should contain 1500 µg/ml K which is added as a solid KCl, except the standards for K which should contain 1500 µg/ml Na as NaCl.

Working standards obtained for Ca, Fe, K, Mg, and Na have the following concentrations of metals (µg/ml): 0.25, 0.50, 1.00, 2.00, and 4.00 µg/ml. For Al the concentrations are 0.75, 1.50, 3.00, 6.00 and 12.00 µg/ml.

The decomposition blank contains 1 ml of aqua regia, 6 ml HF, and 5.6 g H_3BO_3/100 ml.

9.2.2 Cd, Co, Cu, Li, Mn, Ni, Pb, and Zn multi-element standards

Prepare a combined stock standard solution of 506 µg/ml Cd, Co, Cu, Li, Mn, Ni, Pb and Zn from the individual 1000µg/ml stock solutions by pipetting 5 ml of each and diluting to 100 ml with de-ionized water.

Prepare working standards of 0.1-2.0 µg/ml for these elements, except Cd, from the combined stock solution (50 µg/ml) by dilution using the decomposition blank.

For Cd, prepare working standards of 0.5-10 µg/l Cd in the decomposition blank.

9.2.3 Si single element standard

A 1000 µg/ml Si standard is prepared from a pure silica rod by the same decomposition procedure as described for the samples (Section 8.2).

Dilute the 1000 µg/ml stock solution to obtain working standards of 200-400 µg/ml Si in the decomposition blank solution.

9.2.4 Ti single element standard

A 1000 µg/ml Ti standard is prepared from TiO_2 by the same decomposition procedure as described for the samples (Section 8.2).

Dilute the 1000 µg/ml Ti standard to obtain working standards of 2-10 µg/ml Ti.

Make up the working standards in the decomposition blank. Add solid KCl to each standard so that the final concentration is 1500 µg/ml K.

9.2.5 Ba single element standard

Dilute the 1000 µg/ml stock solution to obtain working standards of 0.1-2.0 µg/ml Ba.

Make up the working standards in the decomposition blank. Add solid KCl to each standard so that the final concentration is 1500 µg/ml K.

9.2.6 Be single element standard*

Dilute the 1000 µg/ml stock solution to obtain working standards of 5-30 µg/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 µg/ml stock solution to obtain working standards of 0.1-1.5 µg/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 µg/ml stock solution to obtain working standards of 0.2-3.0 µg/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 µg/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 µg/ml of Na and K are added to a 1 µg/ml Rb standard in the decomposition blank, the enhancement is only about 2% more than in 200 µg/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 3µg/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.

9.2.9 Sr single element standard

Dilute the 1000 µg/ml stock solution to obtain working standards of 0.1-1.0 µg/ml Sr in the decomposition blank as for Ba.

9.2.10 V single element standard

Dilute the 1000 µg/ml stock solution to obtain working standards of 0.3-5.0 µg/ml V in the decomposition blank to which 100 µg/ml Al and 500 µg/ml K have been added to enhance the V absorption. No further enhancement of V has been observed above 100 µg/ml Al and 500 µg/ml K.

9.3 Alternative calibration standards

A preferred alternative means of calibration is to use certified reference materials (CRMs) as calibration standards because the concentration of each metal has been established within a certain degree of confidence. A minimum of 3 sediment or rock CRMs should be chosen for calibration to ensure that the calibration curve generated from the analyses of these materials is correct. The CRMs are prepared and decomposed, and the metals determined in the same way as the unknown samples. A fourth CRM is introduced into the standard and sample set to assess the accuracy of the results.

9.4 Reference Materials

Accuracy of an analytical determination can be established in one of two ways (Veillon, 1986). The first would be to analyze the same sample by two or more independent methods. This is not always feasible. The second would be to analyze reference materials. These are materials whose analyte content has been established by two or more independent methods and whose matrix is as nearly identical to that of the samples as possible.

The sediment reference materials are certified for total metal contents only. Therefore, they can only be used as an accuracy check of the metal concentrations determined in a solution obtained from HF dissolution of the sample.

The samples should not be analyzed until the value obtained from the CRM meets the accuracy requirements for the determination.

For a compilation of working values for 272 geostandards, the reader is referred to a publication by Govindaraju (1989) and recent *IOC Manuals and Guides 25, Standard and Reference Materials for Marine Science Revised edition, 1993.*

NRCC CRM's are available from: Marine Analytical Chemistry Standards Division, National Research Council, Montreal Road, Ottawa, Canada K1A 0R6

NIST CRM's are available from: Standard Reference Material Program, Building 202, Room 204, National Institute of Standards and Technology, Gaithersburg, MD 20899 USA.

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 µg/ml K	Ba, Sr, Ti
	20000X in 1500 µg/ml K	Al, Ca, Fe, Mg, Na
	20000X in 1500 µg/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

(a) Mn and Si are determined directly without any other dilutions.

(b) Solid KCl is added to separate aliquots to give a K concentration of 1500 µg/ml and these are analyzed for Ba, Sr, and Ti.

(c) 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 µg/ml K) matrix. A similar dilution is also made for the determination of K by substituting NaCl as the diluent.

TABLE 3
Standard Conditions For Flame Atomic Absorption Analyses

Perkin-Elmer 4000

Element	Wavelength (nm)	Slit setting (nm)	Background Correction	Oxidant	Reducing flame
Al	309.3	0.7	OFF	N_2O	USE
Ca	422.7	0.7	OFF	N_2O	
Fe	248.3	0.2	OFF	AIR	
K	766.5	2.0	OFF	AIR	
Mg	285.2	0.7	OFF	N_2O	
Mn	279.5	0.2	OFF	AIR	
Na	589.0	0.7	OFF	AIR	
Si	251.6	0.2	OFF	N_2O	USE
Ti	365.3	0.2	OFF	N_2O	USE
Ba	553.6	0.2	OFF	N_2O	USE
Be	234.9	0.7	OFF	N_2O	USE
Co	240.7	0.2	ON	AIR	
Cr	357.9	0.7	OFF	N_2O	USE
Cu	324.8	0.7	OFF	AIR	
Li	670.8	0.7	OFF	AIR	
Ni	232.0	0.2	ON	AIR	
Pb	283.3	0.7	ON	AIR	
Rb	780.0	2.0	OFF	AIR	
Sr	460.7	0.7	OFF	N_2O	USE
V	318.3	0.7	OFF	N_2O	USE
Zn	213.9	0.7	ON	AIR	

9.5.2 Solutions for trace element determinations

For the trace element determinations, the separate 1g sample decomposed in the Teflon bomb is also initially diluted to 100 ml (100X dilution).

From this solution, Be, Cd, Co, Cr, Cu, Li, Ni, Pb, V, and Zn are determined directly.

As indicated in section 8.2, 1g/100 ml decomposition requires several days for the separation of a clear layer for the analysis.

9.6. Standard operational conditions
Settings for flame atomic absorption analyses

The standard operational conditions and instrumental settings for the different elements using the Perkin-Elmer model 4000 for atomic absorption analysis is summarized in

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

Pb should be made of uncoated graphite. In earlier work, without the platform, Rantala and Loring, (1980) found that pyrolytically coated tubes were unsatisfactory for Cd as they produced constantly changing sensitivity and performed well only after >100 firings. Findings with platforms made in the laboratory from the grooved end of the tube (Hinderberger *et al*, 1981) confirm that uncoated platforms perform the best. Uncoated platforms are generally not available commercially, but are prepared in the laboratory. Platforms can be made by cutting the two ends of a graphite tube into eight (4 from each end) 7 mm x 5 mm grooved, curved sections as described by Hinderberger *et al*, (1981). For Al, Co, Cr, and Ni, the platforms are made from coated tubes. They can be inserted into either coated or uncoated tubes.

The platform must be centered under the sample introduction hole and visually inspected to ensure that no sample will run off the platform.

9.8.3 Automatic sample introduction

Automatic sample introduction of 20 µl is recommended as it will provide better precision than manual pipetting. The tip of the sampler must be adjusted in such a manner that it will enter far enough into the sample introduction hole of the graphite tube so that no sample solution can creep around the hole. At the same time the analyst must take care that the tip does not touch the platform.

9.8.4 Sample cups

Watch for any formation of air bubbles at the bottom of the sample cups and eliminate them either by emptying the cup and refilling it, or by tapping the cup to drive out the bubbles.

9.8.5 Optimization of the furnace program e.g. Cd

Optimizing the furnace program requires the use of a blank, a standard, and a reference material solution.

The following is an example of the procedure for optimizing the furnace program for Cd determinations.

The Cd concentration of the standard solution should match that of the reference material. Following the thermal conditioning of the tube and the platform as indicated by a low blank reading, the standard and the reference material solutions are run in sequence until the furnace program is optimized (Rantala and Loring, 1987).

The furnace program has been optimized when maximum peak heights are obtained for the standard and the reference material solutions, and the peak height of the reference material solution is within $\pm$ 10% of the standard at the 0.002 µg/ml Cd level (at the linear range).

To assist in optimizing, the following guidelines should be followed:

(a) Drying: The platform requires a relatively high drying temperature of approximately 270°C. Ramptime must be sufficiently slow to avoid spattering of the sample.

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

(c) Atomization: The fastest possible ramptime 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

Tube 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.

The method of standard additions is unnecessary as direct calibration with standards can be used. We do not recommend the method of additions because it is time consuming and can produce imprecise and inaccurate results (Slavin, 1988; Tyson, 1984)

9.10 Combined analytical scheme

A combined analytical scheme utilizing both FAAS and GFAAS with appropriate dilutions is shown in Table 5 for sediments containing natural levels of heavy metals. Initial solution: 0.2g/100 ml.

TABLE 5
Combined Analytical Scheme for FAAS and GFAAS Determinations

Element	Further dilution in H_2O*	AAS Mode
Cd	NIL	GFAAS
Co	NIL	GFAAS
Cr	10X	GFAAS
Ni	NIL	GFAAS
Pb	NIL	GFAAS
V	10X	GFAAS
Al	10X**	FAAS
Cu	NIL	FAAS
Fe	25X	FAAS
Li	NIL	FAAS
Mn	NIL	FAAS0
Zn	NIL	FAAS

* Initial dilution = 0.2g/100 ml
**KCl solution. Final matrix 1500 µg/ml K

9.11 Relative accuracy and precision

Tables 6 and 7 show the relative accuracy of the major and trace element data for the marine sediments: MAG-1, BCSS-1, MESS-1, PACS-1 and rock samples BIR-1, DNC-1 and W-2 by comparison of values with certified or consensus values reported. Precision is expressed as a standard deviation of the mean value.

TABLE 6
Major and Minor Constituents of Standard Reference Materials

Oxide	PACS-1		W-2		BIR-1		DNC-1	
	%	sd	%	sd	%	sd	%	sd
Al_2O_3	*12.19*	*0.12*	*14.83*	*0.28*	*15.19*	*0.19*	*17.94*	*0.24*
	12.23[c]	0.22	15.35[cs]	0.23	15.35	0.51	18.30	0.49
CaO	*2.84*	*0.01*	*10.98*	*0.06*	*13.35*	*0.19*	*11.40*	*0.20*
	2.92	0.13	10.87	0.29	13.24	0.29	11.27	0.22
Fe_2O_3	*6.98*	*0.04*	*10.60*	*0.09*	*11.14*	*0.12*	*9.84*	*0.08*
	6.96	0.12	10.74	0.23	11.26	0.23	9.93	0.14
K_2O	*1.51*	*0.02*	*0.60*	*0.01*	*0.012*	*0.004*	*0.20*	*0.00*
	1.50	0.09	0.63	0.02	0.027	0.010	0.23	0.02
MgO	*2.48*	*0.02*	*6.24*	*0.05*	*9.44*	*0.13*	*9.96*	*0.19*
	2.41	0.09	6.37	0.18	9.68	0.28	10.05	0.33
Na_2O	*4.45*	*0.03*	*2.18*	*0.01*	*1.77*	*0.04*	*1.87*	*0.03*
	4.40	0.11	2.14	0.12	1.75	0.11	1.87	0.09
SiO_2	*55.27*	*0.19*	*52.47*	*0.50*	*47.94*	*0.45*	*47.16*	*0.35*
	55.70	0.50	52.44	0.64	47.77	0.51	47.04	0.64
TiO_2	-----		*1.06*	*0.01*	*0.94*	*0.03*	*0.48*	*0.01*
			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).

TABLE 7.
Trace Element Concentrations in Standard Reference Materials

Elements	MAG-1[cs] mg/kg	sd	MESS-1[c] mg/kg	sd	BCSS-1[c] mg/kg	sd	PACS-1[c] mg/kg	sd
As	9.2	1.2	10.6	1.2	11.1	1.4	211	11
	–		–		–		–	
Ba	479	41	–		–		–	
	480	28	–		–		–	
Be	3.2	0.4	1.9	0.2	1.3	0.3	–	
	3.6	0.1	–		–		–	
Cd	0.20	0.03	0.59	0.10	0.25	0.04	2.38	0.20
	0.19	0.01	0.59	0.05	0.25	0.01	2.25	0.10
Co	20.4	1.6	10.8	1.9	11.4	2.1	17.5	1.1
	19.3	1.9	–		–		17.7	0.5
Cr	97	8	71	11	123	14	113	8
	112	3	72	1	–		106	1
Cu	30	3	25.1	3.8	18.5	2.7	452	16
	31	4	27	0.6	19.5	0.8	441	6
Hg	–		0.171	0.014	0.129	0.012	4.57	0.16
	–		0.179	0.006	0.153	0.009	–	
Li	79	4	–		–		–	
	78.6	0.5	44.9	0.6	46.5	0.5	33.6	0.5
Mn	760	70	513	25	229	15	470	12
	–		–		–		–	
Mo	1.6	0.6	–		–		12.9	0.9
	–		–		–		–	
Ni	53	8	29.5	2.7	55.3	3.6	44.1	2
	–		–		–		44.5	1.4
Pb	24	3	34	6.1	22.7	3.4	404	20
	28	5	31.1	1.1	23.7	2.6	362	6
Rb	149	6	–		–		–	
	152	2	–		–		–	
Sb	0.96	0.1	0.73	0.08	0.59	0.06	171	14
	–		–		–		–	
Se	1.16	0.12	0.34	0.06	0.43	0.06	1.09	0.11
	–		–		–		–	
Sn	3.6	1	3.98	0.44	1.85	0.2	41.1	3.1
	–		–		–		–	
Sr	146	15	–		–		277	11
	133	3	–		–		–	
V	140	6	72.4	5.3	93.4	4.9	127	5
	145	4	–		–		130	1
Zn	130	6	191	17	119	12	824	22
	133	3	180	2	112	1	839	21

cs = Consensus mean values for MAG-1 (Gladney and Roelandts, 1988b)
c = Certified values for MESS-1, BCSS-1, and PACS-1 (NRCC). Mercury values were decertified for MESS-1 and BCSS-1 in 1990 by NRCC.
Numbers in the second row are values obtained by Rantala and Loring, 1978, 1980. Loring and Rantala, 1992.

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. CHEMICAL PARTITION OF SEDIMENTS: ACETIC ACID (HOAc) EXTRACTION OF SEDIMENTS

Chemical partitioning of metals in sediments is used to provide information on the sources and environmental pathways of the major and trace metals.

Heavy metals, along with other elements, are introduced into estuarine environments in solution and as part of or in association with, solid particles from natural and anthropogenic sources, mainly via rivers, but sometimes through outfalls and dumping. Very little is known, however, about the carriers and transport modes of these particulate metals or their response to estuarine conditions.

Measurement of total sediment or particulate metal concentrations is a poor method of determining such characteristics because part of the metal load is loosely bound to the particles and part is locked up physically and/or chemically in detrital particles and minerals. Selective chemical methods using acetic acid (Loring, 1978), weak HCl solutions (Luoma and Jenne, 1976), and even sequential extractions (Tessier *et al.*, 1979) have been developed and used to partition the total metal concentrations into their loosely bound (non-detrital) and residual (detrital) phases. **It should be noted that all these extraction methods are strictly operationally defined.** Sequential extractions are, in particular, time consuming and of limited value because they fail to provide reliable information on metal partitioning (Nirel and Morel, 1990)..

The acetic acid method was chosen because it is one of the weakest chemical treatments that can be used to remove effectively the weakly bound part of metal concentrations in sediments (Loring, 1978; Loring and Rantala, 1988) and particulate matter (Loring and Asmund, 1989; Loring *et. al*, 1983, 1985). Acetic acid (25% v/v) removes metals held in ion exchange positions, easily soluble amorphous compounds of iron and manganese, carbonates, and metals weakly held in organic matter. It leaves the silicate lattices intact and does not attack the resistant iron and manganese minerals or organic compounds.

The proportion of the total metal concentration removed by the extraction is operationally defined as the non-detrital (acid soluble) metal fraction of the sediment.

The proportion of a metal remaining in the residual fraction is operationally defined as the detrital (acid insoluble) fraction of the material.

Such fractionation allows some deductions as to the carriers, transport mode and potential bio-availability of metals entering and within these different systems (Loring, 1981, Loring *et al.*, 1985).

10.1 Apparatus and reagents

10.1.1 Laboratory equipment

Centrifuge.
Mechanical shaker.
Analytical balance.
Agate mortar and pestle.

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 dessicator 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;

(n) By flame or graphite furnace AAS; analyze the acetic acid soluble and residual solutions for trace metals.

10.3 Atomic absorption analyses

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

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

10.3.1 Apparatus and equipment

Same as for sediments.

10.3.2 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., HOAc, KCl, NaCl, or H_20.

10.3.3 Reference Materials

No reference materials are certified for weak or strong acid solutions.

10.3.4 Flame AAS determinations

(a) Mn, Cu, Li, and Zn are determined directly from solution, but further dilutions are made if required to bring the metal concentrations to the linear portions of the calibration curves.

(b) Solutions for Fe, Ca, and Mg, and Na determinations are diluted 10X with the KCl solution with a final concentration of 1500 µg/ml K.

(c) Solution for K determinations is diluted 10X with the NaCl solution with a final concentration of 1500 µg/ml Na.

10.3.5 Graphite furnace determinations

(a) Solutions for Al determinations are diluted with H_2O 10X or more to bring the concentrations to the linear portions of the Al calibration curve.

(b) Cd, Cu, Ni, and Pb are generally determined directly from solution.

(c) Uncoated L'vov platforms are used for Cd and Pb determinations.

(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.

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 H_3BO_3 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:
Total Zn concentration = 5µg/g + 75µg/g = 80µg/g

11. FLAMELESS ATOMIC ABSORPTION ANALYSIS FOR MERCURY (Hg)

The method used is a modified form of that used by Hatch and Ott (1968). It consists of oxidizing the sediment sample (10-500 mg dry weight) by digesting it with a mixture of concentrated nitric acid (HNO_3) and sulfuric acid (H_2SO_4) at 60 °C for 1 hour and reducing Hg to its elemental state with stannous chloride ($SnCl_2$). The mercury vapor is then passed through a quartz absorption cell of an AAS where its concentration is measured and recorded by means of a strip chart recorder.

NOTE: Mercury and its compounds are difficult to analyze at low levels in environmental samples. Consequently a newly prepared Revision 1 of Reference Method 26 (UNEP/IAEA: Determination of total mercury in marine sediments and suspended solids by cold vapour atomic absorption spectrophotometry) is currently in preparation to address this problem and the attention of the reader is drawn to this document.

11.1 Apparatus and reagents

11.1.1 Apparatus

Atomic Absorption Spectrometer.
Mercury Hollow Cathode Lamp.
Recorder 10 mV full deflection.
Absorption Cell. Constructed from borosilicate glass tubing, 25 mm o.d. X 15 cm with quartz windows (25 mm x 2 mm thickness). Gas inlet and outlet ports attached 2 cm from each end.
Varian, 0 to 120 volts for controlling pump speed.
Pump with peristaltic pumping head.
Water bath.
Aerator: Perkin- Elmer.
BOD bottles.
Tygon tubing.
Digital pipetter 100-1000µl.
Sulfuric acid desiccator: Made by snipping a diffuser from a Perkin-Elmer aerator so that it extends about halfway into a standard BOD bottle. The bottle is filled within 1 cm of the aerator tube with concentrated sulfuric acid (Kothandaraman and Dallmeyer, 1976).

11.1.2 Mercury system setup

The mercury system is assembled by attaching Tygon tubing as follows: aerator → sulfuric acid desiccator → absorption cell → pumphead → aerator. When the aerator is attached to the reaction vessel (BOD bottle) a closed system is obtained. After removing the aerator from the reaction vessel, mercury remaining in the system is vented out by means of an exhaust fan.

11.1.3 Reagents

Nitric acid	[HNO_3]	Concentrated (low in Hg).
Sulphuric acid	[H_2SO_4]	Concentrated (low in Hg).
Stannous chloride	[$SnCl_2$]	10% w/v in 6N HCl.

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 HNO_3 followed by 20 ml of concentrated H_2SO_4. 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% HNO_3 and 0.01% $K_2Cr_2O_7$ (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% HNO_3 and 0.01% $K_2Cr_2O_7$.

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.

11.5 Determination of mercury

Adjust the atomic absorption settings: Wavelength 253.7 nm; slit 0.7 nm; background corrector On.

Prior to analyses, find the aeration rate that gives the best absorption by turning the variac while aerating 1 ml of the 0.1 µg/ml Hg standard. This setting does not need to be adjusted again although a new portion of tubing needs to be placed in the pump head when lower absorption readings are observed for the standards.

(a) Pipette 10 ml of stannous chloride solution with a fast delivering pipette into the cold sample solution in the BOD bottle;

(b) Attach the aerator immediately and observe the sample peak height on the recorder;

(c) When it reaches a plateau, detach the aerator and rinse it with water;

(d) After the peak falls back to baseline, continue with the next sample;

(e) Standards should be run at even intervals between the samples.

11.6 Calibration curve

The calibration curve is constructed by plotting peak height versus µg Hg (standards). The amount of Hg in the unknown samples is read from that curve. The µg Hg found from the curve is converted into µg/g Hg in the sediment by the sample weight in grams.

11.7 Relative accuracy and precision

Accuracy of the analyses was established by the use of certified reference materials (NRCC Marine sediments BCSS-1 and MESS-1). Certified values for BCSS-1 and MESS-1 are 0.129 ± 0.012 µg/g Hg and 0.171 ± 0.014 µg/g Hg, respectively. Values obtained by this method ($n = 6$) are 0.153 ± 0.009 µg/g Hg for BCSS-1, and 0.1769 ± 0.006 for MESS-1. However, NRCC has recently decertified BCSS-1 and MESS-1 for mercury because of suspected contamination. In their place, NRCC has certified a new estuarine sediment BEST-1 for mercury with a value of 0.092 ± 0.009 µg/g Hg. For BEST-1, we obtained a value of 0.095 ± 0.006 µg/g Hg. BEST-1 was replaced in 1994 with MESS-2 which has the same Hg content as BEST-1.

12. DETERMINATION OF READILY OXIDIZABLE ORGANIC MATTER

Organic carbon matter is determined to assess the role played by the organic fraction of sediments in the transport, deposition, and retention of trace metals.

The readily oxidizable organic carbon content is determined by the Walkey-Black method (1947), adopted and modified from Jackson (1958, p.219-221). This method differentiates humus matter from extraneous sources of organic carbon such as graphite and coal. Gaudette *et.al.* (1974) found that this method provided excellent agreement with the LECO combustion method of organic carbon analysis.

The Walkey-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 $Fe(NH_4)_2SO_4$ $6H_2O$ 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).

NOTE: The color of solution will progress from an opaque green-brown, to green upon the addition of approximately 10 ml of the ferrous solution. The color will continue to shift upon titration to a bluish-black-gray; at this point the addition of 10-20 drops of ferrous solution will shift the color to a brilliant green giving one-drop end point.

12.3 Calculation of results

% organic matter (readily oxidizable) = 10(1-T/S) X F
S = standardization blank titration, ml of ferrous solution
T = sample titration, ml of ferrous solution
F = factor derived as follows:
F = (1.0 N) X 12/4000 X 1.72 X 100/sample weight = 1.03 when sample weight is exactly 0.5 grams
Where 12/4000 = meq wt. carbon and 1.72= factor for organic matter from carbon.

NOTE: In the back titration, the ferrous solution reduces the dichromate that has not been used up in the oxidation processes. Therefore, if it takes less than 4 ml of the ferrous solution to reach the end point, then more than 8 ml of the available 10 ml of dichromate has been consumed in the oxidation. If this is the case, then it is necessary to repeat the determination using less sediment.

12.4 Standardization of organic carbon determinations

Dextrose ($C_6H_{12}O_{16}$) is used as the standard. It should contain 39.99% carbon.

(a) Weigh out exactly 0.01 g of dextrose and treat in the same manner as the sediment sample;

(b) The carbon in dextrose is calculated as follows: %C= 10(1-T/S) x F;

F= (1.0N) X 12/4000 X 100/sample weight = 30 for 0.01g of dextrose.

The theoretical value is 39.99% C in one gram of dextrose.

Following standardization with dextrose it is recommended that a well homogenized sample be analyzed and be used for standardization instead of dextrose.

12.5 Precision of determinations

Replicate analyses (10) of a sample with an average of 0.36% organic matter gave a standard deviation of 0.04% (coefficient of variation of 11%). At a level of 3.17% organic matter the standard deviation was 0.05% (coefficient of variation of 1.6%).

13. DETERMINATION OF CALCIUM CARBONATE

Carbonate is often an important component of marine sediments and has been found to be an important indicator of provenance and dispersal of terrigenous material in the Gulf of St Lawrence (Loring and Nota, 1973)

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;

(h) After 2 hours, remove tube C and weigh;

(i) Calculate loss of weight in grams (P);

(j) Repeat the procedure using 100 mg of $CaCO_3$ instead of the sediment and calculate the loss of weight in grams (Q).

13.2.1 Calculation of calcium carbonate content

% $CaCO_3$ = P/Q X 0.100/ weight of dry sediment X 100

NOTE: Tubes filled with $CaCl_2$ should be stored in a desiccator and the $CaCl_2$ replaced if it is observed to be hard.

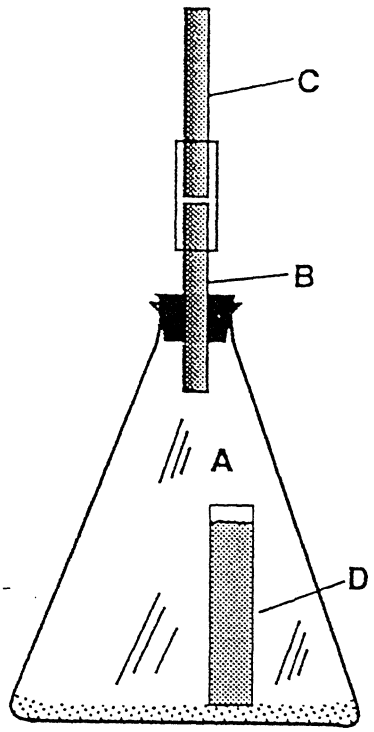


FIGURE 3: Apparatus used for the determination of $CaCO_3$. A = Flask; B = Rubber stopper fitted with glass tube filled with $CaCl_2$; C = Second glass tube filled with $CaCl_2$ attached to tube B by means of plastic tubing; D = Vial filled with 4N HCl.

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 <u>essential</u> 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 $\pm$ 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.

14.1.1 Filter holders

Polycarbonate filter holders for 47 mm diameter Nuclepore filters with plastic fittings and air vents such as the Millipore Swinnex , Nuclepore or Sartorius model SM16541B are all suitable. Since the filter holders are reused, they must be thoroughly cleaned in the laboratory between each oceanographic cruise. An ultrasonic bath containing laboratory detergent may be used to remove particles that have become attached to the filter holders. The filter holders are then soaked for 24 hours in 6N HCl after removal of the silicon O-rings. The silicon O-rings are soaked for 1 hour in 1N HCl. After rinsing several times in deionized water, the filter holders are then air dried in a clean air bench and loaded with the preweighed filters using plastic tweezers. After their initial use at sea, the filter holders are thoroughly rinsed with deionized water between each use before the preweighed filter is reloaded into the filter holder.

14.2 Collection of SPM samples

The basic collection technique consists of pressure filtration of the sea water through the Nuclepore filters in clean plastic filter holders

Depending on the SPM levels, sample collection procedures will either be direct on line filtration from the Go-Flo, Niskin bottle or other sampler, or an off-line filtration of an initial sample of unfiltered sea-water sample in a separate filtration apparatus.

14.2.1 Off-line filtration

For highly turbid waters, rapid settling of particles in the water sampler results in an underestimation of the true SPM concentrations if sampled directly from the water sampler. To compensate for this problem, about 2 liters or less of unfiltered water is withdrawn from the sampler and filtered separately. To ensure a representative subsample, the water sampler is agitated by inverting it and returning it to its upright position to ensure a uniform distribution of SPM before subsampling. After the subsample is withdrawn, it is then gently agitated again to ensure that the SPM remains in suspension before pouring it into the filtration apparatus. The time elapsed between sampling and filtration must be kept to a minimum.

The off-line filtration apparatus used at BIO consists of a 500 ml polypropylene separatory funnel that has been adapted for pressure filtration by welding a fitting for a pressure line into the lid. A preloaded Sartorious (model SM16541B) filter holder is attached to the bottom of the funnel with a short piece of silicone tubing. An aliquot of the unfiltered water is poured into the funnel, the top is screwed on and the pressure applied. An air filter is placed in the nitrogen gas line to prevent the introduction of particulate contamination through the line. The sample is filtered until the filter clogs or all of the water sample has been passed through the filter.

For water samples containing much less than 0.5 mg/l of SPM, an on-line filtration procedure is used because insufficient sample is collected by the off-line filtration procedure unless large quantities of water are processed.

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 (0.2μm) Milli-Q water while ap6plying 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.

14.5.3 Reagents

Hydrofluoric acid	[HF]	(46%).
Nitric Acid	[HNO_3]	(71%).
Hydrochloric acid	[HCl]	(37%).
Aqua Regia:	[HNO_3- HCl]	(1:3 v/v).

Boric acid crystals.
High purity water (Milli-Q or De-ionized reverse osmosis water).

Ultra-high purity grade acids equivalent to the J.T.Baker Ultrex grade must be used for the SPM decomposition because the reagent grade acids contain large amounts of Fe and Si. Boric acid crystals can be of ACS analytical reagent grade.

14.5.4 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 1 mg (dry weight) is usually required to determine most of the metals at their natural background levels.

14.6 Total decomposition procedure

(a) Using plastic tweezers, transfer a filter into a Teflon bomb and squash it into the bottom of the vessel;

(b) Add 1 ml of aqua regia, 1 ml of HF and close the bomb tightly;

(c) Submerge the bomb in boiling water for 1 hour, or heat for 45 seconds in a microwave oven (For further details see section 8.2).

(d) After cooling, decant the contents through a polypropylene funnel into a 25 ml polypropylene volumetric flask containing 0.93 g of boric acid and approximately 5 ml of water.

(e) Wash the filter remaining in the Teflon bomb several times with small volumes of water, each time collecting the washings in the 25 ml flask (some broken pieces of the filter may enter the flask, but will settle and do not interfere with subsequent metal determinations);

(f) Finally, shake the volumetric flask to complete the dissolution and make up to 25 ml with de-ionized water;

(g) Prepare the blank solution in the same manner, omitting the sample;

(h) Store the solutions in polypropylene bottles;

(i) Analyze the solutions for trace metals by flame or graphite furnace AAS.

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 H_2O 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 H_2O.

(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.

14.7.4 Flame AAS determinations

(a) Si, Mn, Cu, Li, and Zn are determined directly from solution;

(b) Solutions for Fe, Ca, Mg, and Na determinations are diluted 10X with the KCl solution with a final concentration of 1500 µg/ml K;

(c) Solution for K determinations is diluted 10X with the NaCl solution with a final concentration of 1500 µg/ml Na;

(d) Further dilutions may be required to bring the metal concentrations into line with the linear portions of the calibration curves;

(e) Si, Ca, and Mg are determined in the N_2O-acetylene flame;

(f) The other metals are determined in the air-acetylene flame.

14.7.5 Graphite furnace determinations

(a) Solutions for Al determinations are diluted with H_2O 10X or more to bring the concentrations into line with the linear portion of the calibration curve;

(b) Cd, Cu, Ni, and Pb are generally determined directly from solution;

(c) Uncoated L'vov platforms are used for Cd and Pb determinations because they provide better sensitivity than the coated platforms;

(d) Coated L'vov platforms are used for Al and Ni determinations;

(e) No platform is used for Cu because greater sensitivity is provided by using a pyrolytically coated tube.

14.7.6 Furnace control program steps

The furnace controller programs used are shown in Table 4 (Section 9.8.5). 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) Internal argon flow is reduced to 50 ml/min during atomization. The gas interrupt mode is used for low levels of Cd.

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.

14.10 Extraction procedure

(a) Center the sample filter and lay it flat on the moistened filter support;

(b) Screw the filtration funnel tightly on to the base and insert the glass rod into the silicone tubing;

(c) Attach the filter holder base to the receiver flask;

(d) Place 5 ml of 25% v/v acetic acid in the funnel;

(e) Cover the funnel and let it stand for 24 hours;

(f) After 24 hours, remove the glass rod and quickly insert the silicone tubing into a 10 ml volumetric flask placed in the receiver flask (no loss of acetic acid solution from the tubing before its insertion into the flask will occur unless the filter has been pierced or badly seated on the support);

(g) Apply vacuum to the receiver flask;

(h) After all the acetic acid has been filtered, wash the filter twice with 2 ml of water, each time applying vacuum;

(i) After the final wash, remove the funnel and transfer the filter to a Petri dish for drying at 60 ^{o}C;

(j) Under vacuum, suck the rest of the filtrate trapped in the filter holder into the flask;

(k) Make the flask up to a volume of 10 ml with water, transfer the solution into a polypropylene bottle, and store for AAS analyses;

(l) Treat the Nuclepore filter blanks in the same manner;

(m) Decompose the residual matter on the dried filters with HF + aqua regia (section 12.6);

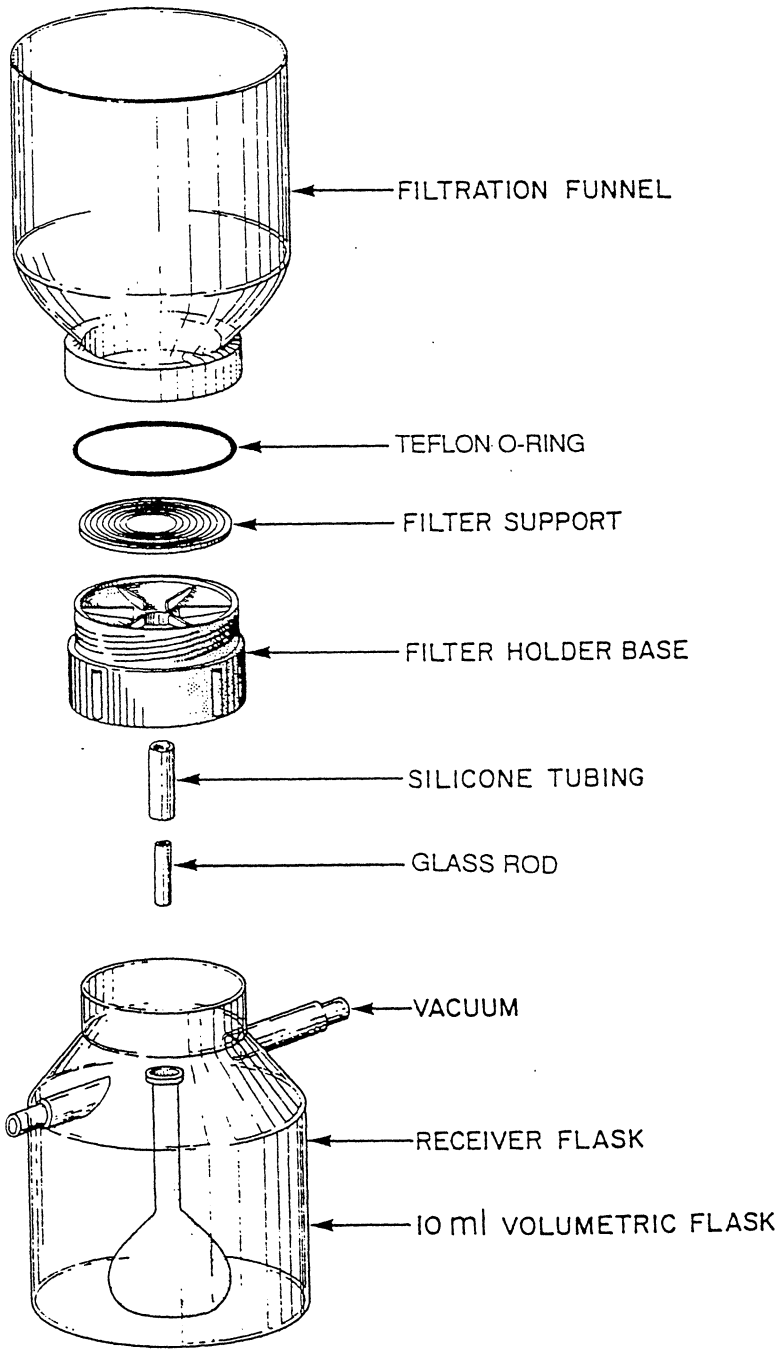


FIGURE 4: Apparatus for Acetic Acid Extraction of SPM (Loring and Rantala, 1990).

14.11 Atomic absorption analyses

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

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

14.11.1 Apparatus and equipment

The same as for sediments.

14.11.2 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. HOAc, KCl, NaCl, or H_2O.

14.11.3 Reference Materials

No reference materials are certified for weak or strong acid solutions.

14.12 Flame AAS determinations

(a) Mn, Cu, Li, and Zn are determined directly from solution, but further dilutions are made if required to bring the metal concentrations into line with the linear portions of the calibration curves;

(b) Solutions for Fe, Ca, and Mg, and Na determinations are diluted 10X with the KCl solution with a final concentration of 1500 µg/ml K;

(c) Solution for K determinations is diluted 10X with the NaCl solution with a final concentration of 1500 µg/ml Na;

(d) Ca and Mg are determined in the N_2O-acetylene flame. The other metals are determined in the air-acetylene flame.

14.13 Graphite furnace determinations

(a) Solutions for Al determinations are diluted with H_2O 10X or more to bring the concentrations into line with the linear portions of the Al calibration curve;

(b) Cd, Cu, Ni, and Pb are generally determined directly from solution;

(c) Uncoated L'vov platforms are used for Cd and Pb determinations;

(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 H_3BO_3 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.

TABLE 9

Results of Intercomparison Exercise(s) for Particulate Metals

1. ICES intercomparison exercise for particulate metals in sea water

Sample	Metal	%	sd	Metal	mg/kg	sd
Fergusons Cove	Al	3.26[O]	0.44	Cd	1.8	1.2
		2.91[C]	0.41		3.5	1.6
Bedford Basin		2.56	0.25		1.8	0.3
		2.41	0.41		3.5	1.2
Fergusons Cove	Fe	2.06	0.21	Cu	55	17
		2.55	0.27		64	7
Bedford Basin		2.47	0.21		135	32
		2.49	0.23		100	36
Fergusons Cove	Mn	0.162	0.012	Pb	152	39
		0.168	0.060		121	37
Bedford Basin		0.808	0.116		288	29
		0.780	0.107		220	59
Fergusons Cove				Zn	250	46
					197	60
Bedford Basin					525	41
					417	104

0 = Value of Loring and Rantala, 1992 (n = 4: Sample weight = 0.80 - 1.27 mg SPM on Nuclepore filters)
C = Intercomparison exercise mean value (Yeats and Dalziel, 1987).

2. GEMSI intercomparison exercise for particulate trace metals in riverwater: coordinator H. Windom

Al		Fe		Mn		Cu		Ni		Pb		Zn	
mg/l	sd	mg/l	sd	µg/l	sd	µg/l	sd	µg/l	sd	µg/l	sd	µg/l	sd
4.4[O]	0.5	1.7	0.2	20	3	2.1	0.1	1.9	0.3	1.3	0.2	5.1	0.8
3.5[C]	1.0	1.9	0.3	21	6	1.8	0.6	1.1	0.7	1.0	0.6	5.6	1.9

0 = Value of Loring and Rantala, 1992 (n = 6)
C = Intercomparison exercise mean value.

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°) and western Europe (>52°), 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 2necessary 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.

Three levels of sampling can be used to provide increasing amounts of environmental information.

(a) The first is the simplest and least expensive and involves the use of grab samples (section 4.2.1) of the top surface layer to provide an immediate assessment of the sediment characteristics and the presence or absence of contamination in an area. Relatively undisturbed samples of the sediment surface layer can be obtained if precautions are taken in soft muds to avoid contamination of the samples and to ensure that fines have not been lost on sampler recovery. Since deposition rates cannot be determined from such samples, this approach does not allow an estimate of the time trend, if any, of contamination. Rough baseline levels, as will be discussed later, however, can be established from a grab sample.

(b) Level 2 sampling involves box or core sampling (Sections 4.2.2 and 4.2.3), in which representative samples from successive depths are obtained. This allows more reliable surface and sub-surface samples to be collected from which time trend information can be obtained as well as information on the deposition sequence and the extent of biological mixing of the sediments.

(c) Level 3 sampling is the same as that of level 2 but with the significant addition of radiochemical or other measurements to determine the rate of deposition and biological mixing rates. Such a level of sampling is required to understand the rate and mechanisms of contamination build-up, if any, in the sedimentary environment. In most cases, samples of the most recently deposited sediments, usually the top 1-2 cm, obtained from grab samplers are sufficient to determine the present trace metal concentrations. Since such concentrations may vary with time, short cores (~ 10 cm) sampled at 1 cm intervals will provide sufficient samples to establish trace metal time trends, if any, in fine grained sediments.

15.2.2 Chemical analyses

It is recommended that the whole sample be digested and analyzed. This is because total metal concentrations determine the true extent of metal levels in the sediments. It is the criteria by which the extent, if any, of contamination is evaluated and on which national and international dredging and dumping regulations are based. For example, the Canadian Ocean Dumping Control Act (ODCA) limits dumping material containing > 0.6 mg/kg Cd and >0.75 mg/kg Hg in the total sample.

A size fraction of the total sediment may be used for subsequent analysis if required to determine the absolute metal concentrations in that fraction, providing that its contribution to the total is kept in perspective when interpreting the data. Such size fraction data might be useful in tracing the regional dispersal of metals associated with a specific size fraction, providing the provenance of the material remains the same.

A number of subsamples are required for analyses (Figure 1). A 0.1-1 gram subsample is required for the determination of the total metal concentrations and should be well homogenized.

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.

15.4.1 Simple normalization (Level I)

The simple approach to the normalization of geochemical data for grain size effects is to compare the total metal concentrations of surface grab samples with background levels with those estimated by the means suggested in Section 15.3. Direct determination of metal concentrations in texturally and mineralogically equivalent sediments provides the best background levels. The degree of contamination and time trends of contamination at each sampling location can be improved upon by making a comparison with metal levels in texturally equivalent sub-surface core samples. The texture of the sediments can be roughly classified as to their sandy or muddy nature visually and by feel, or preferably by separation into their sand and mud size components by wet sieving (Section 6.1.). The <53μm fraction was used by Loring and Nota (1973) and Loring (1978) to mark the separation between sand and mud before the <63μm fraction was established as the preferred fraction. The <63μm size fraction is now used and recommended. In the Gulf of St Lawrence (Loring, 1978), for example, muddy silicate sediments containing >70% by weight material <53 μm have average background levels of 0.2 mg Cd/kg, 0.2 mgHg/kg, 21 mgPb/kg, and 85 mgZn/kg. Sandy sediments (> 70% > 53 μm by weight) have total background levels that average 0.1 mg Cd/kg, 0.1 mgHg/kg, 19 mgPb/kg, and 33 mgZn/kg. If a factor 3 is introduced to account for mineralogical variations in background values, it is therefore likely that comparable muddy sediments in this region are significantly contaminated by one or more of the following metals if Cd is >0.60 mg/kg, Hg >0.60 mg/kg, Pb > 63 mg/kg, or Zn is > 255 mg/kg. Conversely, total Cd levels of >0.3 mg/kg, Hg levels of >0.3 mg/kg, Pb levels of >57 mg/kg, or Zn levels of >99 mg/kg in sandy sediments from the region would signify contamination. Such information would allow an immediate rough assessment of the surface contamination and its spatial distribution.

Some estimate of the degree, if any, of contamination can also be calculated by using the so-called index of geoaccumulation (I_{geo}) proposed by Muller, (1979). This index is defined as $I_{geo} = \log_2 Cn/1.5Bn$ where Cn is the measured concentration of the metal "n" in sediment or size fraction and Bn represents the background concentration of the metal "n"-either found in the literature or measured directly in texturally equivalent uncontaminated sediments or size fractions. The factor 1.5 is introduced to account for variations in background values which can be attributed to mineralogical variations in the sediments.

It should be emphasized that the validity of the background values and enrichment factors will depend on the accuracy of the background term i.e., the direct measurements of background values either in texturally equivalent sediments or size fractions are more accurate than values obtained from the literature.

15.4.2 Mathematical normalization (Level II)

It is necessary to reduce or eliminate grain size effects on chemical data from different samples in order to deduce the real trends rather than those superimposed by grain size effects. In this approach, it is assumed that the relationship between the metal such as Zn and particle size or a proxy for particle size in the sediment is linear. The idea being that, should the concentration of the metal be related to changing sediment particle size, the concentration will change with a constant relation to grain size or its proxy. For linear mathematical normalization to be of value, the following requirements should be met:

(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 $<53\mu m$ 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.

Data points falling inside the 95% confidence band would be considered to be part of the natural population whereas those outside would be considered to belong to an anomalous population. For example, an anomalous Zn/mud ratio occurring outside the graphed prediction bands is easily identified in Figure 5. Such samples with anomalous metal: grain-size ratios do not necessarily indicate anthropogenic inputs as they might be the result of plotting errors, analytical errors, or anomalous concentrations of detrital heavy minerals containing the metal, such as Cr bearing magnetite or chromite. Such normalization for grain size, of course, is of little value if the grain size of the sediments containing the trace metals is essentially the same, or a selected grain size fraction is used. In both cases, the variability of the trace metal concentrations reflect mineralogical and source variability, but in the latter, the contribution to the total sediment is also an important consideration.

15.4.4 Metal : reference metal normalization

Metal : reference metal normalization can be used in addition to, or in lieu of grain size normalization. The assumption is that the reference metal used such as Al or Li represents a certain mineral fraction of the sediments such as the use of Al as a proxy for the granular variations of the aluminosilicate fraction, particularly the clay fraction, or a specific mineral or mineral group such as the use of Li as a proxy for micas, and/or the clay minerals (Table 10). If a metal proxy for grain size such as Al or Li is used in conjunction with grain size data, then it should be established that Al or other reference metal varies significantly with grain size before it is used. The normalizing element must, therefore, be an important constituent of one or more of the major fine-grained trace metal carrier(s) and reflect their granular variability in the sediments. They are "conservative" in that they have a uniform flux from crystal rock sources and so compensate for changes in the input rates of various diluents or variations in sedimentation rates.

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

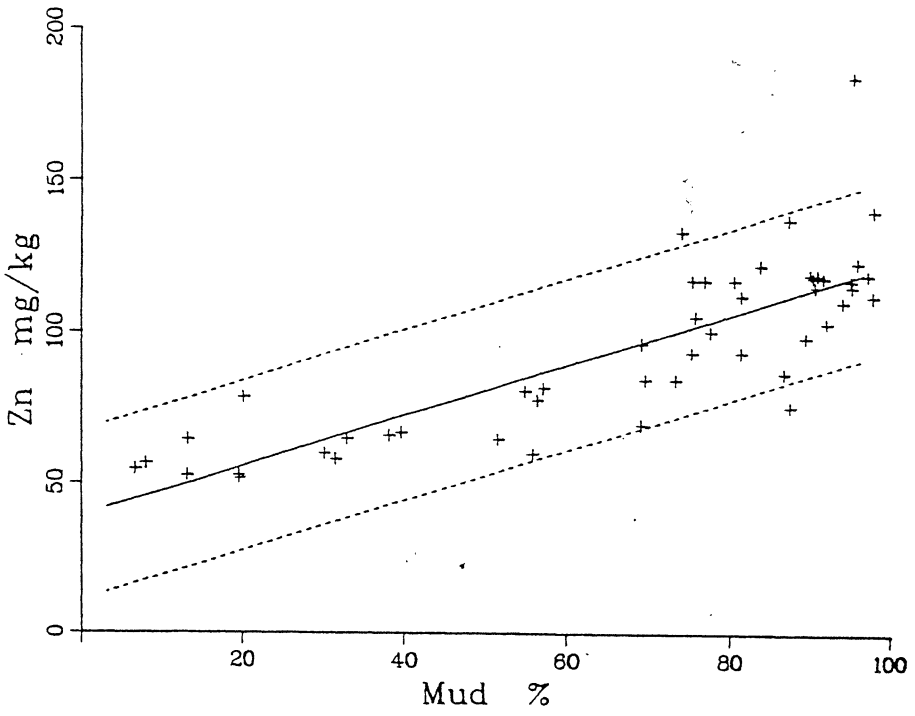


FIGURE 5. Zn : mud scatter plot for the St. Lawrence estuary (n=49; r=0.82). Solid line represents the regression line. Parallel dashed lines define the 95% confidence band. Data from Loring, 1978.

In many cases, separate determinations of the grain size distributions are not made or not deemed necessary and a metal proxy for granular variations such as Al and/or Li is used instead . This approach is valid and Al has been successfully used by Windom et al., (1987) and many others for normalization of sediments that have not been derived from the glacial erosion of igneous rocks. It has been shown, however, that Li (Loring, 1990) is superior to Al for the normalization of trace metal data from glacial sediments and for the identification of anomalous metal concentrations. Lithium determinations are also both precise and accurate by FAAS (Rantala and Loring, 1990).

The close statistical covariance of the metal distributions with Li and grain size rather than Al for such glacial sediments can be demonstrated from direct determinations of the trace metals, Li, and Al in individual sediment size fractions from different parts of the Gulf of St Lawrence (Loring, 1989). Figure 6 shows, for example, the close covariance of Zn with Li but not with Al concentrations as the metals increase with the decreasing size fractions. The close covariance of Li and Zn with changes in the size fractions in this case, reflects the increase in the Li and Zn bearing minerals with decreasing grain size. The spread of Li concentrations and Zn within each fraction reflects the effects of mineralogical differences (provenance) on the granular Li and Zn distribution.

Figure 6 illustrates the use of Li for normalization of Zn data from the St Lawrence estuary. This scatter plot of Zn versus Li was constructed and a regression line with the 95% confidence band graphed to define the natural geochemical population of Zn in relation to the normalizer element Li in the sediments. The confidence band was included to indicate a 95% probability that the points that fall within the prediction interval belong to the normal population and those outside belong to an anomalous population.

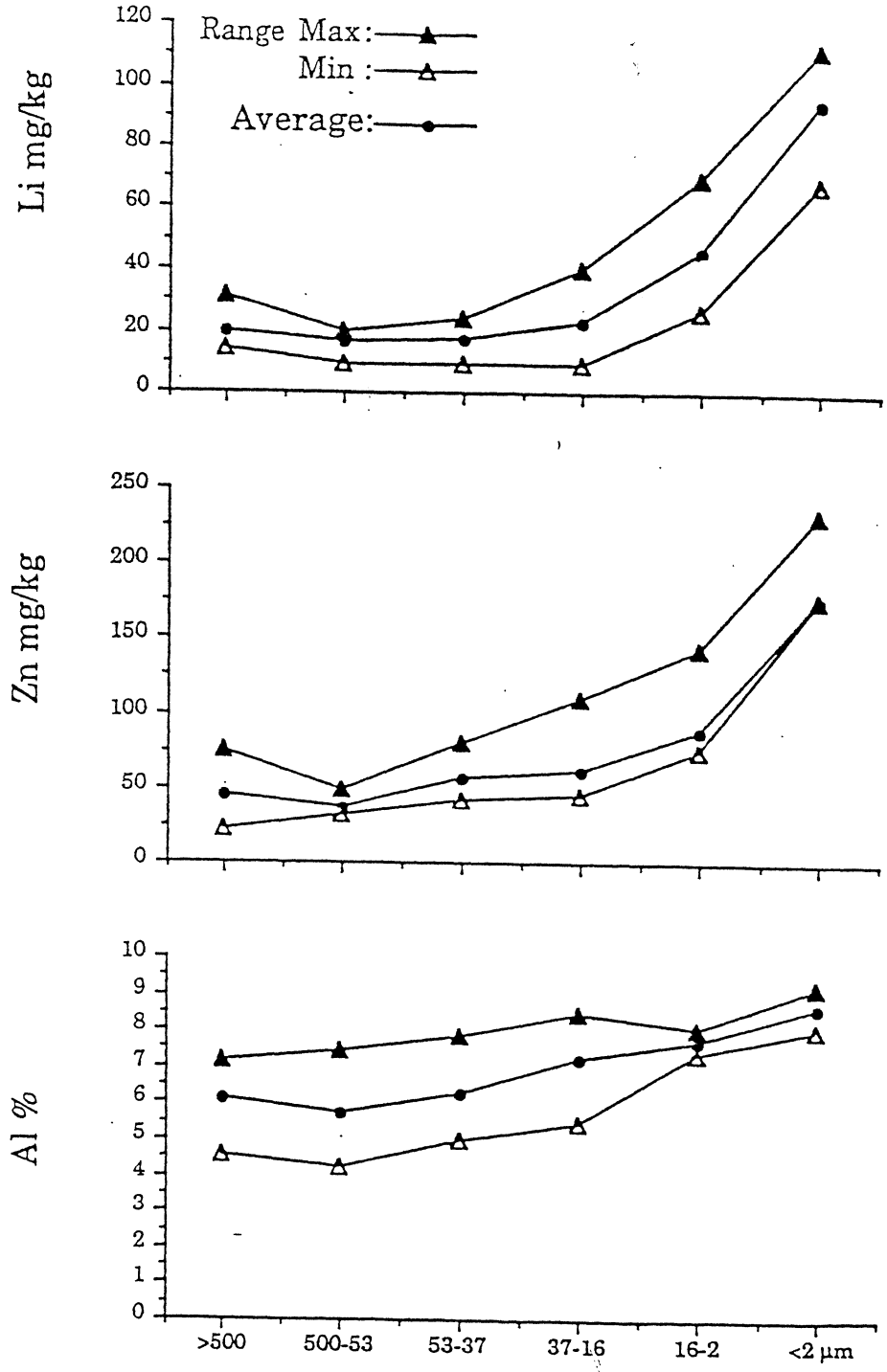


FIGURE 6: Changes of Li, Zn, and Al concentration with size in 18 samples from different parts of the Gulf of St. Lawrence. Data from Loring, 1978.

Figure 7 shows that Zn varies significantly ($r = 0.87$, $p < 0.001$, $n=49$) with Li (Loring, 1990) within a narrow confidence band. The choice of Li as a proxy or normalizer for size variations in grain size can be confirmed by its significant correlation with mud content ($r = 0.88$, $p < 0.001$, $n=49$) as with Zn (Fig. 5) in these sediments.

In order to use such a scatter graph as in Figure 7 to identify anomalous values of Zn, for example, in other samples from this area it would be necessary to:

(a) Define and remove any outlier values from the data set representing the natural metal population;

(b) Recalculate and graph the trimmed data set;

(c) Determine the Li and Zn concentrations at other sites;

(d) Plot the Zn versus Li data on the scatter plot.

Data points falling inside the 95% confidence band would be considered to be part of the natural population where as those outside would be considered to belong to an anomalous population. For example, an anomalous Zn/Li ratio occurring outside the graphed prediction bands is easily identified in Figure 7. Firstly, it should be determined if the anomalous ratio is real and not an artifact of the analysis. If real, its presence would suggest that one of the sediments is influenced by anthropogenic inputs although the possibility of a natural enrichment of a Zn mineral carrier could not be ruled out without further investigation.

One of the major disadvantages is that the metal/Li or any other reference element normalization yields a ratio value instead of a real concentration. This can be overcome in varying degrees by standardizing the contents to a reference material and defining an enrichment factor.

The relative enrichment of Zn or any other metal can be estimated by standardizing anomalous metal values to those in some background reference sediment. For example, an enrichment factor of Zn relative to Li can be defined from (Zn/Li sample) (Zn/Li reference sediment).

The validity of such an enrichment factor varies with values used for the reference material. Most authors have used values for crystal abundances which are of little value because they do not represent the regional background levels and because of the analytical uncertainty in their measurements. To be of any value, the reference ratio must represent the material for which a comparison is required.

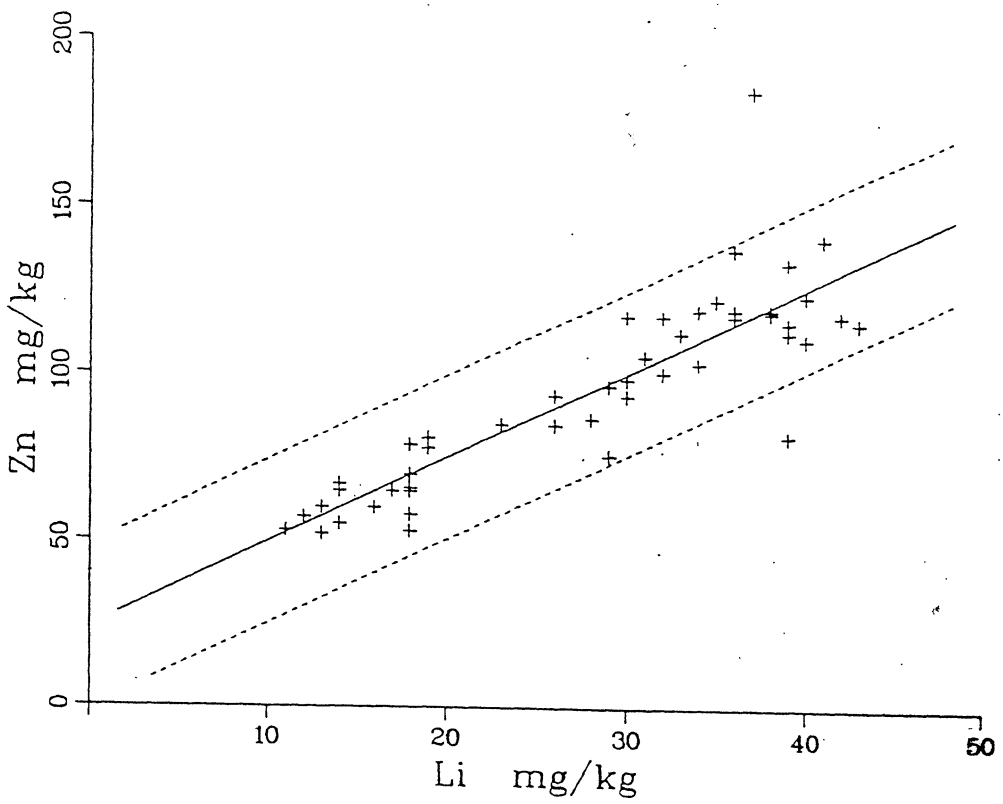


FIGURE 7: Zn: Li scatter plot for the St. Lawrence estuary (n=49: r=0.87). Solid line represents the regression line. Parallel dashed lines define the 95% confidence band. Data from Loring, 1978.

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.

Geochemical studies that involve the determination of major elements and heavy metals, grain size parameters, organic matter, carbonate , and mineralogical composition in the sediments are, however, more suitable for determining the factors that control the trace metal distribution than measurement of absolute trace metal concentrations in a specific size fractions or the use of metal/reference metal ratios alone. This is because such studies can identify the factors that control the trace metal variability in the sediments.

16. BASIS FOR OBTAINING QUALITY DATA

Guidelines for data acquisition and data quality evaluation in environmental chemistry were published by UNEP (Reference Method 57) and by the American Chemical Society (ASC, 1980). The following remarks are based on these guidelines.

16.1 Planning

It is extremely difficult to achieve accurate results in environmental analysis. It is of utmost importance that every step of the analytical programme is well planned. Such a plan or model is implicit or explicit in every measurement process. Data are generated in order to answer specific questions and to draw usable conclusions. If the data generated are not responsive to the questions posed, then the conclusions will be faulty even if the data are accurate. Thus the model or plan must be based on a collaborative effort by the analyst, who is an expert in the measurement techniques, the scientist who will use the data and the statistician who will help to evaluate the data. No measurement programme should be undertaken until such a plan is developed which includes the statement of the problem, the sampling and analytical protocols, and the statistical methods that will be used in data evaluation.

16.2 Quality assurance

A quality assurance programme must be established by every analytical laboratory, it should be designed to assess accuracy and precision and to identify and correct problems as they arise. General elements necessary to quality assurance programmes can be listed as follows:

1. Maintenance of skilled personnel, written and validated analytical methods, and properly constructed and equipped laboratories.
2. Acquisition of representative samples and controls.
3. Acquisition of high quality analytical standards for instrument calibrations.
4. Use of high quality and/or dedicated glassware, solvents and other reagents and equipment.
5. Routine calibration and adjustments of instruments and maintenance of continuous records of these calibrations.
6. Routine performance tests including complete procedural blank analyses and standard recovery experiments.
7. Use of reference materials with certified values.
8. Regular and critical review of analytical results.
9. Use of replicate samples.
10. Comparison of results with other laboratories (intercomparison).
11. Response to user complaints.

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 (X), and the standard deviation (s) and then plot the following values on a blank control chart:

X, X+2s (UWL), X+3s (UCL), X-2s (LWL) and X-3s (LCL).

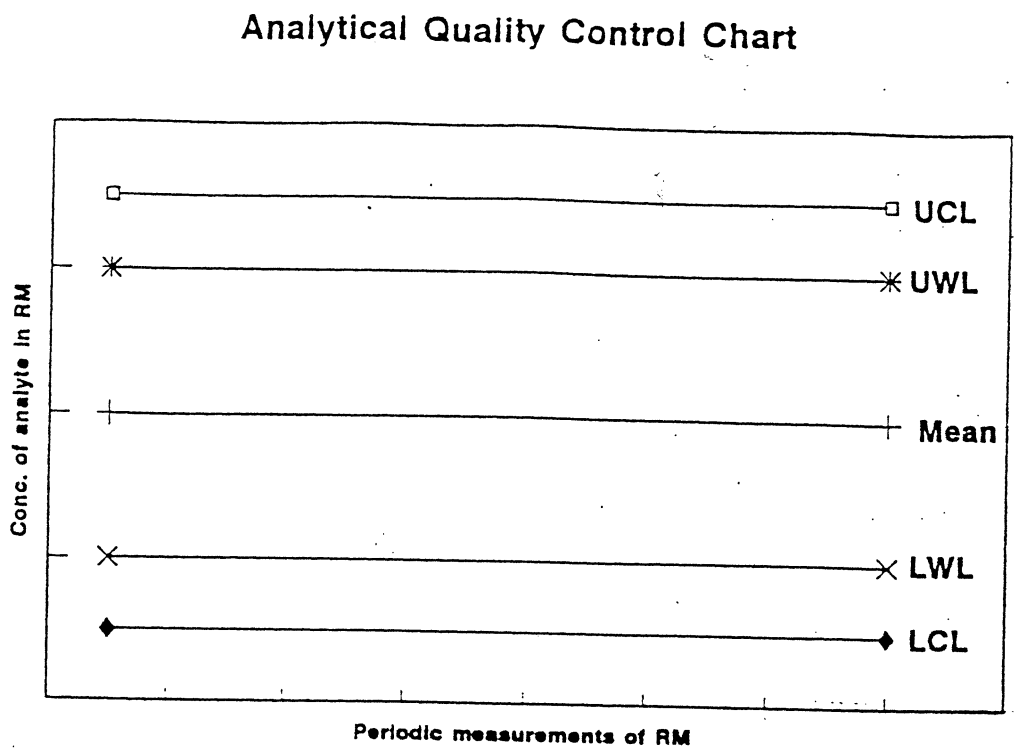


FIGURE 8: Blank control chart.

16.3.3 Using an AQCC

Assuming that the analytical measurements for RM(s) follow a normal distribution, 95% of them (19 in every 20) should fall within the area between UWL (upper warning limit) and LWL (lower warning limit). Similarly 99.7% of the results should fall within the area between UCL (upper control limit) and LCL (lower control limit).

The analyst should plot the results of the analysis of RM(s) after each batch of analyses to check where the data lies in relation to these limits. An example of such a plot is given in Figure 9.

The following guidelines can be used to assess whether the data for the RM(s) and consequently the data for the samples are of acceptable quality, i.e., are the analyses under control?

(a) The mere fact that one result falls outside the warning limits need not require the analyst to doubt the result or take any action provided that the next result falls within the warning limits.

(b) If the results fall outside the warning limits too frequently, particularly if the same warning limit has been crossed more than once on consecutive results, then the analyst needs to assess the source of this systematic error.

(c) If the results on more than 10 successive occasions fall on the same side of the X line (either between X and UWL or X and LWL) then the analyst needs to check the analytical procedure to determine the cause of this error.

(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.

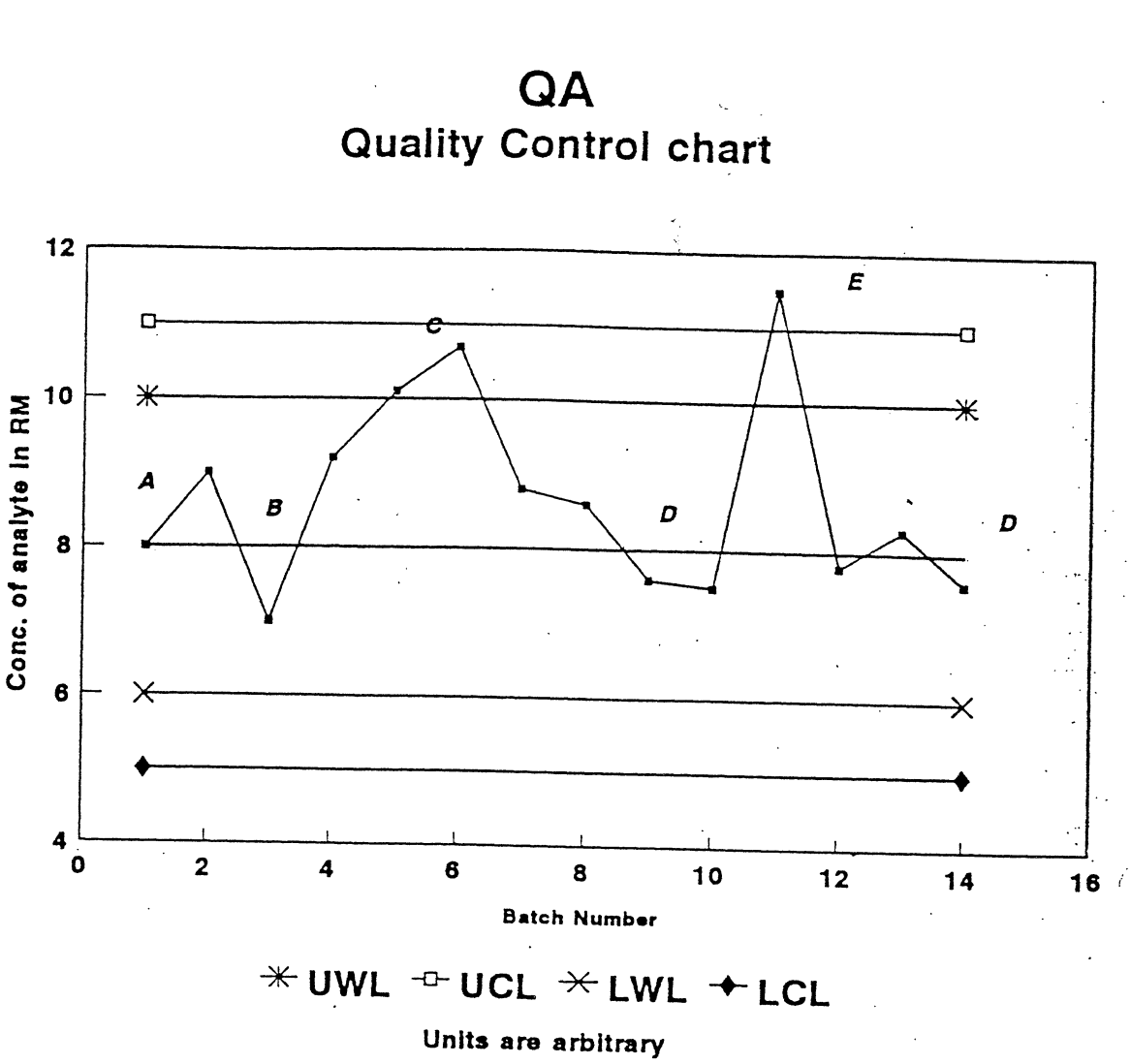
16.4 Definitions of some relevant statistical terms

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).



ANNOTATIONS

(A) A "consensus value" is established by repeated analyses of an IRM. Upper and lower warning limits are determined statistically from the standard deviations (s) of the n measurements made.

(B) The routine measurements of the IRM are well within the warning limits. Measurements are under control.

(C) Something appears to be contaminating the samples here. Reagents were investigated and a new batch of solvents was found to be at blame and was replaced immediately.

(D) The process is back under control.

(E) Here, a serious problem was discovered. The previous ten data were rejected and all analyses were discontinued until the fault (dirty glassware this time) was detected and corrected.

FIGURE 9: An Example of a Quality Control Chart.

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