

A COMPENDIUM OF THE SAMPLING AND  
ANALYTICAL TECHNIQUES USED BY THE  
ENVIRONMENTAL MARINE GEOLOGY  
SUBDIVISION, AGC, BIO

by

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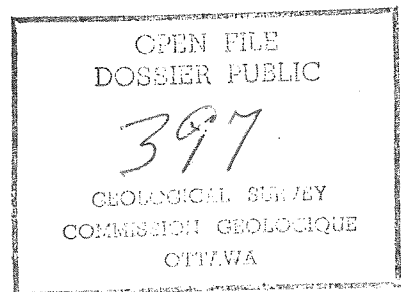
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A COMPENDIUM OF THE SAMPLING AND ANALYTICAL TECHNIQUES USED BY  
THE ENVIRONMENTAL MARINE GEOLOGY SUBDIVISION, ATLANTIC GEOSCIENCE  
CENTRE, BEDFORD INSTITUTE OF OCEANOGRAPHY, DARTMOUTH, NOVA SCOTIA

COMPILED AND EDITED BY

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A COMPENDIUM OF THE LABORATORY AND SAMPLING TECHNIQUES USED BY ENVIRONMENTAL  
MARINE GEOLOGY, ATLANTIC GEOSCIENCE CENTRE, BEDFORD INSTITUTE OF OCEANOGRAPHY,  
DARTMOUTH, NOVA SCOTIA

INTRODUCTION

This Compendium has been compiled for circulation in order to provide information about techniques that have been found to be reliable by Environmental Marine Geology personnel. The objective of this work is not to establish these techniques as the only methods, but rather to present the techniques now recognized and used by this institution. In keeping with this idea, the Compendium's form is one which enables it to be modified or changed and it makes allowance for the addition of new techniques. It is a dynamic notebook rather than a static record.

The techniques are described in a basic, operational style. Little effort has been made to explain all the theoretical implications of the techniques or to present arguments in their favour. However, with each technique the references to specific studies and papers have been included to enable the reader to further his understanding of the technique. The Compendium is styled also with the assumption that those using it are familiar with general laboratory procedures, so cleaning techniques, contamination prevention methods, common laboratory ware use and the operational instructions for commercially-supplied instruments are not included. Except where otherwise noted, the reagents and equipment used are widely attainable good laboratory grades and quality.

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## SUBAQUEOUS SEDIMENT SAMPLING METHODS

ABSTRACT: The three types of subaqueous sediment sampling commonly employed are dredge sampling, grab sampling, and core sampling. Dredge sampling results in a large, disturbed sample (fine material is washed out) from the upper layers of the sediments. Rocks and molluscs are often studied using dredge samples. Grab samples result in smaller less disturbed sediment samples from the superficial layers of the bottom. Grabs are easiest to use and require the least equipment. Core samplers are the only samplers that collect sediments below the superficial layers. Core samplers are more difficult to use, but result in less disturbed samples, with, however only a limited amount of sediment available at each depth for testing.

DREDGE SAMPLING: The dredge used for collecting rocks is a square metal box with a bag made of chain replacing one end. It is available in several sizes. This dredge is most often used for sampling rock outcroppings on slopes on the bottom. A large boat is required with equipment for dragging the dredge.

The dredge used for collecting molluscs consists of a metal framework covered with fine but strong net, with vertical bars spaced at the mouth to permit entry of molluscs but prevent entry of larger rocks. Again, a large boat is necessary.

The sand sampler is a stainless steel cone with a hole in the end covered by a cloth bag. It is used only for sandy sediments. The sampler is dragged along the bottom and the bag retains the sand and allows the water to pass through. Another version of the sand sampler is a solid conical bucket which is also dragged along the bottom. The excess water is poured off. The sand sampler is not used in deep water.

GRAB SAMPLING: Four types of grab samplers commonly used are: The Eckman, Shipek, Van Veen and Dietz-Lafonde. All are composed of essentially a set of jaws that snap shut upon reaching the bottom.

The Eckman grab is the favored grab for inshore work, resulting in moderate sized samples. It can be used for any kind of sediments except sand or gravel, which stick in the jaws and cause washing out of sample during the ascent to the surface. The Eckman is light enough to be handled by hand, and so requires only a small boat, or in shallow water, no boat at all. The jaws of the Eckman are forced open and held with the release mechanism. The grab is then lowered slowly to the bottom. When bottom is reached, the line slacks off, and the Eckman is usually lifted and redropped a few feet away, to ensure that it has not landed on its side. A messenger weight sent down along the line from the surface strikes the release mechanism and causes the jaws to snap shut. Weights are usually placed on the Eckman, but its position in deep water or currents still remains uncertain. The messenger system ensures that the jaws do not shut until the operator wishes them to. The sample obtained is reasonably undisturbed, and surface and subsurface samples can often be taken from it.

The Shipek grab sampler results in the<sup>least</sup> disturbed sample of any of the grabs, and can be used in any depth of water. It is useful for sampling muds, silts, and sands, and it is also a reasonably successful sampler for sediments which contain both fine and coarse material, because it has a side closure, so there is very little loss of fine material even when the jaws are not completely closed. The Shipek is heavy, and requires a boat with a winch, to raise and lower it. Moderate size samples are obtained with this grab. The Shipek is operated on the same principle as the Eckman, except that its jaws are essentially the two halves of a cylinder split lengthwise. One is forced open, against a spring, until it rests inside the other, where it is held with the release mechanism. The release mechanism is designed so that it trips when the wire slackens when bottom is reached. There is little danger of washing out of sediments during the ascent to the surface, even when a rock is caught in the jaws because of



the side closure. Surface and subsurface samples can be taken from the Shipek sample. Because the Shipek contains its own trip weight, it will occasionally trip and close before reaching the bottom when the motion of the boat is sufficient to remove tension from the wire.

The Van Veen sampler results in a large sample and is primarily used in deep water. It can be used for any type of sediments. A boat with a winch is required, for raising and lowering it. The Van Veen can be obtained in different sizes. The samples taken are disturbed, but it is usually possible to take surface and subsurface samples from them. Some washing out of sample may occur while it is being brought to the surface. The chief problem with the Van Veen sampler is the release mechanism. The jaws are opened and hooked together on top. When they strike bottom, they open further and release the hook. However, in the lowering process, the wave action may provide enough push from underneath to open the jaws far enough to set off the release mechanism. In this case, the jaws close in midwater.

The Dietz-Lafonde grab sampler results in a very small, disturbed sample. It can be used for any type of sediments, but usually not in deep water. Although fairly heavy, it is small enough to be used by hand. It has two jaws with a release mechanism that closes the jaws when it hits bottom. Most of the sample is retained in the grab while it is being removed to the surface. The Dietz-Lafonde is useful for tests such as size analysis, but it risks contamination of sediments for chemical tests, because of the small size and the disturbance of the sample. The Eckman grab is used in place of the Dietz-Lafonde wherever possible. The Dietz-Lafonde is often used in the Arctic because it is small enough in diameter to fit through holes drilled in ice. A modification in the trigger mechanism is necessary to facilitate the retrieval of the tripped grab through ice. By hinging the trigger so that it will hang

loosely and vertically after it is activated, the grab can be hauled through smaller ice openings.

CORE SAMPLING; Core samples are divided into four categories: diver, gravity, piston cores and vibrocores.

Diver cores are the favored cores, but can only be used at depths up to about 80-100 feet. The advantage of the divers core is that the diver can select the exact location, and make sure that a complete core is obtained. The divers core has a plastic barrel  $2\frac{1}{2}$ " in diameter, with a device to hammer it into the sediments. Cores 4 to 5 feet long can be obtained. Unlike other cores, the divers core will go through sand layers as well as silt and mud. A small boat is the only equipment required, except close to shore where no boat is needed at all. The diver takes the core down with him, and hammers it into the sediments. The top of the core barrel is capped when it is filled, and a rope from the boat is fastened to it. The diver signals the surface to have the core pulled up, and the lower end of the core barrel is capped as it clears the bottom. The divers core ensures an undisturbed core.

Piston and gravity cores are heavy and usually require larger boats with winches. They are used in deeper waters than divers cores are, and generally result in larger samples than it is possible to obtain with divers cores. As core barrels increase in diameter, ease of penetration into the sediments decreases. But at the same time, larger and more representative samples at each depth are obtained.

The difference between a piston and a gravity core is the presence of a piston, or cylinder which fits inside the piston core. The piston sits inside the lower end of the core barrel during lowering, after the core hits the sediment, the core barrel slides past the piston into the sediment. The piston aids in the penetration by creating suction, hence, much longer cores can be

obtained by piston coring than by gravity coring. Piston cores generally are less compacted than gravity cores because of this suction, however the uppermost few centimetres of a piston core are disturbed because of contact with the piston. A short gravity core is sometimes used as a trip weight for a piston core so that the sediment-water interface can be sampled along with the piston core sample.

Some types of piston and gravity cores used and their distinguishing features follow. The Alpine core is a gravity core resulting in cores 1½" in diameter and 5 -6 feet long. The long box core is another gravity core with a rectangular core barrel. Different sized barrels are available, but they are all made up of two sections screwed together at opposite corners of the barrel. The advantage to this is that one side of the barrel can be removed, and undisturbed samples taken directly from the core. The LeHigh core is also a gravity core, used primarily for muds. It has a core barrel 6" in diameter and 10 ft. long.

The sphincter core is a piston core with a free fall device. Its core barrel is 4.5-5" in diameter. The core catcher for the sphincter core is a wire that surrounds the core and pulls tight with a purse string effect. The Benthos model 2450 core is a piston core, also with a free fall device. The core barrel comes in ten foot lengths which can be put together, up to five in total, to give the desired core length.

Some Alpine cores can also be used as piston cores. Piston cores of 20 m length can be obtained.

The Vibrocorer is a relatively new sampling method and hence it is described in greater detail than the other coring methods. EMG uses the larger of the two size, the 20 foot, 2 ton model. The Vibrocorer has the capability to sample sandy sediments in deeper water than Diver Cores

The service of a large ship with adequate winching power is necessitated by the size of the Vibrocorer. The Vibrocorer is composed of a fixed frame which guides a free-moving barrel and the electrically powered, vibrator pot. On lowering the Vibrocorer to the sampling point by steel wire, the vibrator is activated which reduces the wall friction on the barrel. The barrel is able to penetrate the sediment by gravity fall. Sediment distortion within the tube is reduced by a piston and a plastic sleeve. A trigger is activated to close the gate at the base of the core to seal in the sample. A winch on the frame is used to return the pot and barrel to the start position and the ship winch hoists the Vibrocorer to the surface.

Throughout the coring operation, the Vibrocorer's penetration, pitch, roll and electrical power usage are monitored by six channel brush recorders on board the ship.

SPECIAL PROBLEMS AND SUGGESTIONS WITH THE VIBROCORER: Slopes may not be sampled with the Vibrocorer. An upright position is maintained on retrieval to insure undisturbed samples. A resonating effect is attained by turning the Vibrocorer on and off thus enabling the barrel to penetrate cobble sediments.

Hydrostatic pressure is responsible for occasionally pushing the piston up the tube after air becomes trapped in the barrel at the surface. Sample size is reduced, therefore.

REFERENCES: Amos, C.L., Long, B. and Schafer, C.T., 1976. CSS DAWSON Cruise Report 76-074(2), B.I.O. Report Series.

Bouma, A.H., 1969. Methods for the study of sedimentary structures. John Wiley and Sons Inc., New York.

Buckley, D.E., 1973. Environmental marine geology of the Strait of Canso and Chedabucto Bay, Port Hawkesbury, Nova Scotia. B.I.O. Field Report 75-022.

There are three common types of sediment samplers: Dredge, Grab and Core.

The following table illustrates the differences.

	EQUIP. REQ.	DEPTH TYPE
<b>DREDGES:</b>		
Rock	Ship, crane, winch	Large, boulders, shells
Coarse fine	Ship, crane, winch Boat, by hand	Small to large shells Gravel, silt, mud
<b>GRABS:</b>		
Eckman	Boat, by hand	Silt, mud
Shipek	Ship, sm. winch*	Sand, silt, mud
Van Veen	Ship, sm. winch*	All types dependent on size
Dietz LaFonde	Boat, sm. winch*	Sand, silt, mud
<b>ORES:</b>		
Leathos	Ship, crane, winch	Silt, mud
Alpine	Ship, crane, winch	Silt, mud
Hubbs	Ship, crane, winch	Mud
Long	Ship, crane, winch	Sand, silt, mud
Hyver	Boat, 2 SCUBA divers	Sand, silt, mud

\* e.g. Hydrographic Winch

## SUBSAMPLING TECHNIQUES AND STORAGE

ABSTRACT: The Environmental Marine Geology subsampling system is designed for the best use of the collected samples. The analyses to be performed determine the subsampling methods and the storage requirements.

PROCEDURE: An opening meeting is convened to set the goals of the operators of a multidisciplinary study. Sample usage is planned and priorities are set. In general, a grab sample is made for each department wanting a sample from a particular area.

At the time of collection, the water portion in the grab is drained or siphoned off. The surface and subsurface samples are collected using a small section of a core barrel. The core is pushed out of the barrel from the bottom and the surface is sliced off at measured intervals for labelling and bagging. A plastic vial can also be used, and the surface layer simply scraped off. Bulk samples are taken from the undisturbed centre of the grab with a plastic scoop, then labelled and packaged. Some tests are run immediately, but most samples are containerized and sent to the laboratory. A portion of the field sample is saved for future needs so that updating work can be performed without having to collect a new sample.

Cores which contain excess water are drained through tap holes in the core lines. They are then capped, taped and refrigerated in an upright position. Unusual core features are detected by X-ray analysis. The longitudinal sectioning is performed by cutting down the opposite sides of the core and drawing a taught piano wire through the core. Half is sent to the Archive in a "D"-tube (semi-circular) for storage and the other half is tested.

Treatment of the samples is determined by their end requirements. Geochemical studies are guarded against sources of elemental contamination and

against bacterial action. Teflon or plastic sampling apparatus are used to obtain the first goal, sodium azide (1 ml of 0.1 M  $\text{NaN}_3$ /Kg wet sediment) additions and refrigeration are used to attain the second. Samples for geochemical analyses are not frozen because freezing can cause changes in clay mineral structures which results in damages in the trace metal associations. Samples for size analysis are simply kept cool. Freezing can be used to preserve organic-based samples. X-ray analysis samples cannot be frozen. Orientation of the core samples must be kept constant and recorded for the Paleomagnetic studies. Paleoecology samples are poisoned with 4% Formalin and refrigerated.

DISCUSSION: Because of the difficulty in resampling exact locations, and also because of possible seasonal or other temporal variations in sediments, a subsample of every sediment sample should be saved as a reference sample.

Few metallic components are contributed to the samples by the addition of reagent sodium azide.

If the sediments are frozen, the structure and mineralogy are damaged. Interstitial water composition and sediment trace metal associations may also be altered.

The samples can be humidified and refrigerated to prevent dessication or biological breakdown. The refrigeration is arbitrarily set at  $4^{\circ}\text{C}$  to simulate natural conditions. However, the conditions of oxidation are unavoidably altered during storage.

## ARCHIVE

ABSTRACT: Whenever large numbers of samples are collected, a detailed sample sorting system is required so that, months after collection, all relevant information is available for each sample. Much of this information must be recorded at the time the sample is collected. A well organized data filing system is essential.

DISCUSSION: The Atlantic Geoscience Centre is in a growth and refinement stage with its archival system. Although not all phases mentioned in this report are in effect, they are the contemplated procedures in the operation.

The collected samples of the Atlantic Geoscience Centre operation have been housed in a repository on the grounds of the Bedford Institute of Oceanography. The samples are sorted according to ship and cruise number; and this raw sample data is stored on computer tape. Samples from outside agencies have been put on file and a complementary service has been offered to those contributors under a special distribution policy. The card file system consists of computer printouts from tapes. The tape information is tailored to the job at hand; information is obtained from annual reports, cruise reports and personal records of researchers.

A record of analyses and work performed on the samples is maintained. A prototype field data acquisition system has been designed to get conformity amongst the contributors. At the present time reference is made to the person having done the work and their personal files must be examined to determine what work has been done.

A more complete file on the core work is upcoming. Core descriptions and photography could be included with an up-to-date file on examination results. Cross file checking for information will soon be eliminated so that one call for information from the computer will be all that is necessary.

A link up to the geophysical computer systems, which contain map studies,



is also planned.

DATA BASE FILE STRUCTURE (COLLECTION)

- IDENTIFICATION:
- 1) Record Number
  - 2) Locality Number
  - 3) Year
  - 4) Cruise or Report
  - 5) Sample Type (Coded)
  - 6) Sample Number
  - 7) Scientist (Coded)

POSITIONAL INFORMATION:

- 8) Latitude
- 9) Longitude
- 10) Depth
- 11) Marsden Square
- 12) National Topographic System Co-ordinates
- 13) Universal Transverse Mercator Co-ordinates
- 14) Day
- 15) Time
- 16) Notes

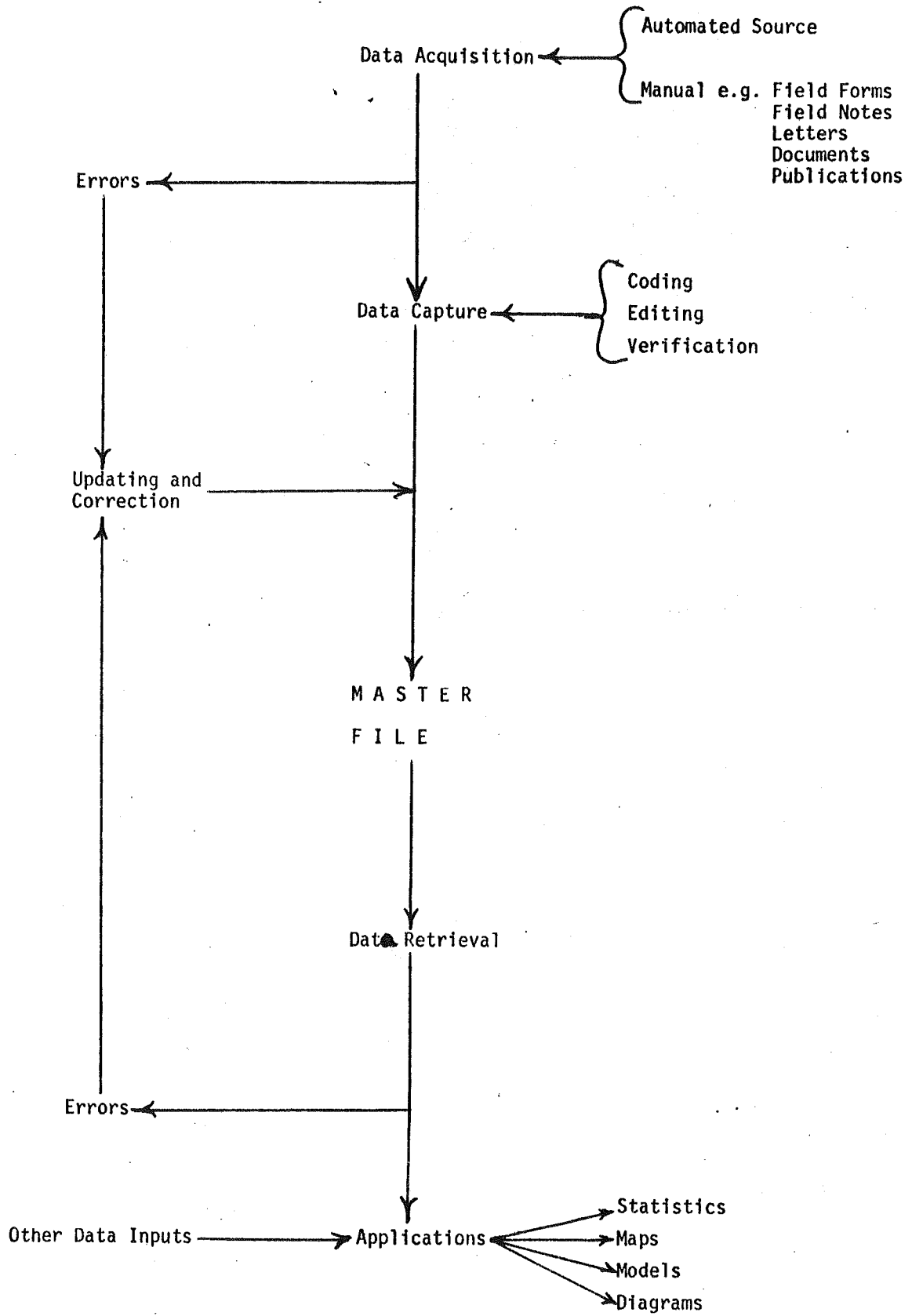
SAMPLE DESCRIPTION:

- 17) Sampler Type
- 18) Number of Subsamples
- 19) Number of Attempts
- 20) Damage (yes or no)
- 21) Munsell Colour Code
- 22) Sample Description
- 23) Related Information
- 24) Notes

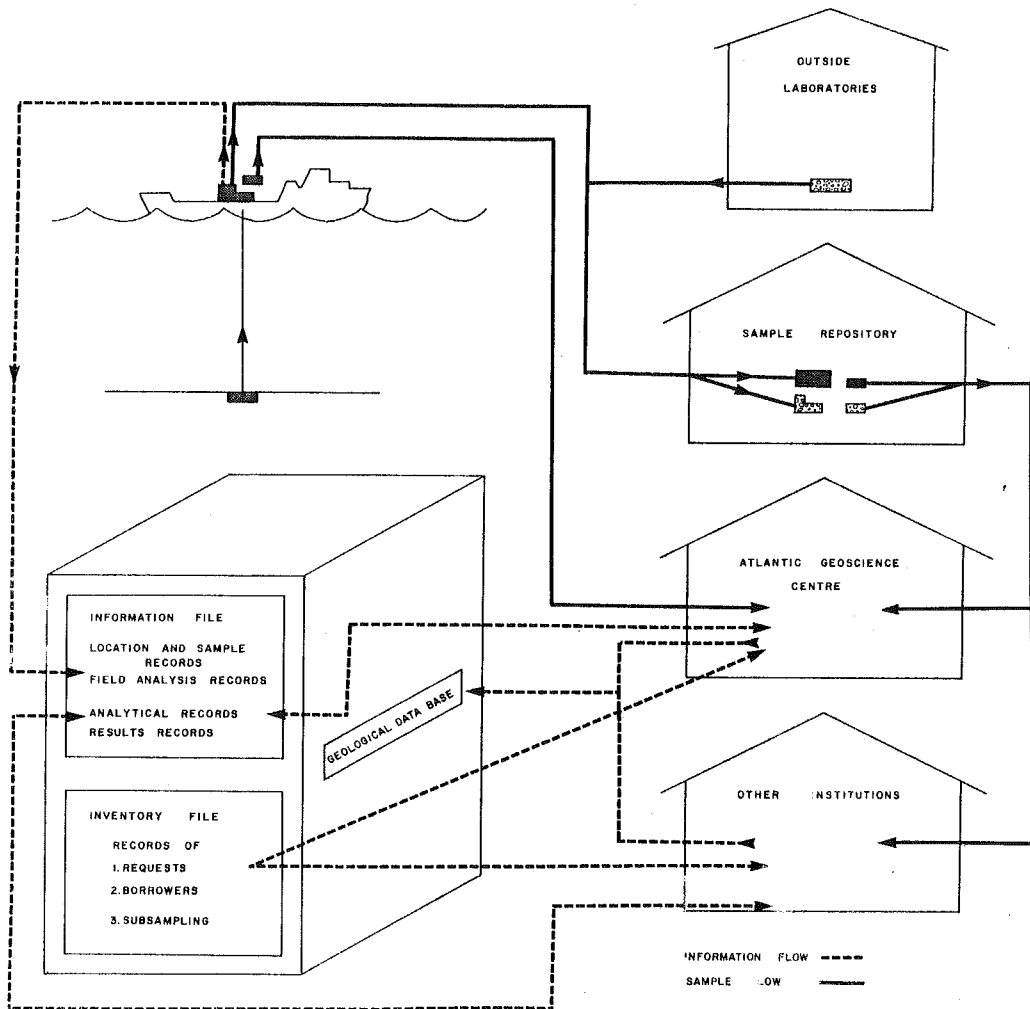
DATA BASE FILE STRUCTURE (ANALYTICAL)

Field Analysis Results	)	
Sediment Size Analysis Results	)	
Micropaleontological Analysis Results	)	Atlantic Geoscience Centre
Geochemical Analysis Results	)	File
Other Pertinent Information	)	
Well Data File	)	

THE ATLANTIC GEOSCIENCE CENTRE FILE MANAGEMENT SYSTEM



# THE ATLANTIC GEOSCIENCE CENTRE DATA SYSTEM



## ANALYSIS OF SEA WATER FOR NINE TRACE METALS

ABSTRACT: This paper describes a chelation-solvent extraction and atomic absorption spectroscopy method for analyzing natural waters for nine trace metals (Al, Cd, Co, Cu, Fe, Mn, Ni, Pb, Zn). A distinction is made between the labile and total metal concentrations. Three chelating reagents (APDC, DEDC, 8-hydroxy quinoline) are added simultaneously to the aqueous sample and the chelated metals are extracted with MIBK.

EQUIPMENT: Separation apparatus (separatory funnels should be Pyrex with Teflon stopcocks)  
Nalgene bottles (or equivalent)  
Filtration apparatus  
Atomic Absorption Spectrophotometer and recorder  
pH meter

REAGENTS: Ammonium pyrrolidine dithiocarbamate (APDC)  
Diethyl dithiocarbamate (DEDC)  
8-Hydroxyquinoline (Oxine)  
Methyl isobutyl Ketone (MIBK)  
Nitric acid  
Deionized distilled water (18 mega ohms per cm)  
Hydrochloric acid  
Ammonium hydroxide

Chelating Reagent: A composite chelating reagent mixture containing 0.5% ammonium pyrrolidine dithiocarbamate (APDC), 0.5% sodium diethyldithiocarbamate (DEDC), and 0.06% 8-hydroxyquinoline (oxine) is prepared for the simultaneous chelation of all nine metals. Five grams each of APDC and DEDC are added to a 500 ml volumetric flask and diluted to volume with deionized water. The solution is thoroughly mixed and filtered to remove any undissolved portions of the salts. The filtrate is purified by three successive extractions with 100 ml portions of MIBK. Oxine (0.6 g) is added to the purified dithiocarbamates and the final combination is diluted to 1000 ml with deionized water. The oxine must be added after the purification of the APDC and DEDC because oxine is extremely soluble in the organic phase. A significant portion of the oxine is

lost from the aqueous phase if it is included in the purification steps.

STANDARDS: Stock standard solutions ( $1000 \mu\text{g ml}^{-1}$ ) for Al, Cd, Co, Fe, Mn, Ni, Pb and Zn are prepared from pure metal dissolved in acidified water. An intermediate composite working standard is prepared from these solutions, and contains  $2.5 \mu\text{g ml}^{-1}$  aluminum,  $1.25 \mu\text{g ml}^{-1}$  iron and manganese,  $0.5 \mu\text{g ml}^{-1}$  cobalt and nickel,  $0.25 \mu\text{g ml}^{-1}$  zinc and copper,  $0.125 \mu\text{g ml}^{-1}$  lead, and  $0.004 \mu\text{g ml}^{-1}$  cadmium. The pH is adjusted to 2.5 with hydrochloric acid.

Standard calibration solutions are prepared by the addition of 0, 2.0, 4.0, 6.0, 8.0, 10.0 ml of the intermediate composite working standard to 500 ml portions of deionized water. The blank solution contains no metal addition. These solutions thus contain 0, 10, 20, 30, 40 and  $50 \mu\text{g l}^{-1}$  aluminum; 0, 5, 10, 15, 20 and  $25 \mu\text{g l}^{-1}$  manganese and iron; 0, 2, 4, 6, 8 and  $10 \mu\text{g l}^{-1}$  cobalt and nickel; 0, 1, 2, 3, 4 and  $5 \mu\text{g l}^{-1}$  zinc and copper; 0, 0.5, 1.0, 1.5, 2.0 and  $2.5 \mu\text{g l}^{-1}$  lead; and 0, 0.016, 0.032, 0.048, 0.064 and  $0.080 \mu\text{g l}^{-1}$  cadmium. The pH of each solution is adjusted to pH 2-2.2. These composite standards are then chelated and extracted using the same procedure that is used for total metal analysis in the samples. From analysis of these standards, a calibration equation is derived (Equation 3) as described in the "Sample Calibration" section which follows.

#### PROCEDURE:

Equipment Preparation: Storage containers which are commonly used are "Bel-Art" polypropylene bottles. These containers should be leached with concentrated nitric acid for at least one hour, and thoroughly rinsed with deionized water ( $18 \text{ M ohm cm}^{-1}$  specific resistance). The bottles are then filled with deionized water and stored until required. At the moment of sample collection the deionized water is drained from the container. This container is then thoroughly rinsed with the incumbent sample prior to filling and retention. At this point the sample is poisoned and stored as noted below.

Concentrated hydrochloric acid is used to clean the separatory funnels, the filtration apparatus and the glassware. The acid residue is removed by three to five rinses of all the equipment with distilled water. The atomic absorption spectrophotometer with a recorder is set up, calibrated and operated in accordance with the manufacturer's manual, exceptions noted in Table II. For the lead and cadmium analysis, an electric arc furnace is used to atomize the samples. The machine is also set up in accordance with the manufacturer's manual using the Peak Mode. Both operations employ the recorder.

Sample Preparation: It is recommended that samples be stored for a minimum period of time. However, if sampler must be stored for an extended time period, changes due to biological activity and chemical reaction can be retarded by the addition of  $10^{-4}$  moles  $\ell^{-1}$  sodium azide (1 ml of  $10^{-1}$  M  $\text{NaN}_3/\ell$  sample) followed by storage in a cold room at  $4^\circ\text{C}$ .

In the laboratory sample preparation varies depending upon whether the labile or total trace metal concentration is to be determined. 500 ml portions of the aqueous samples are transferred to 1000 ml separatory funnels. If only the labile metal (that present in a readily available form) is to be preconcentrated for analyses, the samples are not pretreated and the chelating reagent is added at the natural pH of the aqueous sample. Total trace metal analyses requires that the metals in the sample first be dissociated. This is accomplished by addition of hydrochloric acid sufficient to adjust the pH to approximately pH 2. This must be done 24 hrs before the addition of the chelating reagent.

A 25 ml volume of the composite chelating reagent is added to the 500 ml aqueous sample (in the 1000 ml separatory funnel) and dispersed by shaking. If the sample is first acidified (pH 2), the pH is raised to pH 8.2 with ammonium hydroxide, and a second 25 ml portion of the chelating reagent is then added. This is again dispersed, and allowed to stand for five minutes. To each

separatory funnel is added 25 ml of MIBK followed by vigorous shaking for a minimum of 30 seconds. The emulsions are allowed to stand five minutes followed by a repeated shaking. After a 10-minute separation interval, the aqueous phase is drained into an acid-cleaned Nalgene bottle. The organic layer is transferred to 50 ml glass test tubes and set aside for later atomic absorption analyses.

The aqueous portions are returned to their respective separatory funnels and a final 25 ml portion of mixed chelating reagent is added, dispersed, and extracted with MIBK as described above. Immediately following completion of the second extraction, both sets of solvent extractants are analyzed for the nine trace metals. The efficiency of extraction for each element is given in Table 1.

Instrumental Analyses: Determination of the nine trace elements recovered from all aqueous solutions is made by atomic absorption spectrometry using recommended settings except as noted in Table 1. For Fe determinations an absorption wave length at 273 nm was chosen as it was found to be well separated from other spectral lines and gave good sensitivity.

An air-acetylene 'oxidizing' flame, in conjunction with a three-slot (Boling) burner, was used for all determinations except Al, Pb and Cd. For Al, a nitrous oxide-acetylene 'oxidizing' flame was required. Samples were aspirated at a rate of 5.5-6.0 ml min<sup>-1</sup>. The flameless attachment for atomic absorption (heated graphite furnace) was used for Pb and Cd analyses because of the improved sensitivity.

Instrumental parameters for the analyses of samples preconcentrated by the optimum chelation solvent extraction procedure are reported in Table 1.

Sample Calibration: A regression equation is used to calculate results. Two successive chelation-solvent extraction preconcentration steps are used in the



analytical procedure to ensure a maximum recovery of the metal from the aqueous phase. It is necessary to combine the analytical results of the two procedures and to mathematically account for the effects of background absorption and reagent impurities. Brewer, et al . (1969) devised a standard additions method, using two successive preconcentration steps, and was able to distinguish between the metal concentration of the original sample and a significant blank concentration caused by light scattering and impurities from the reagents and glassware.

A typical chelation solvent extraction calibration plot of absorption signal,  $Y$ , versus metal standard additions,  $X$ , is shown in Figure 1. A linear regression least squares line was fitted to the points. The equations of the lines representing the first and second analytical preconcentration curves are  $Y_1 = A_1 + B_1X$  and  $Y_2 = A_2 + B_2X$ , respectively.  $A_1$  and  $A_2$  are absorption signals of the blank calibration solution ( $X = 0$ ). This blank absorption signal is the sum of the background absorption,  $Y_R$ , and the absorption caused by reagent impurities ( $X_R B_1$  and  $X_R B_2$ ). The slopes of the lines are  $B_1$  and  $B_2$ .  $X_R$  is the concentration of metal contamination and is described below.

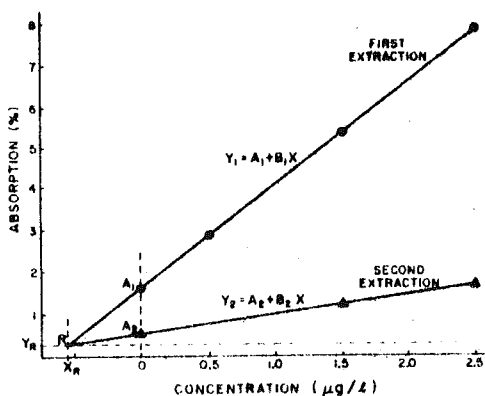


Figure 1. Standard calibration curves for atomic absorption analyses of the extracted samples.

Extrapolations of the two lines through points  $A_1$  and  $A_2$  intercept at point R. The co-ordinates of point R  $(X, Y)$  represent the standard addition extrapolated value  $X_R$  due to acid and base contamination introduced by adjustment of pH, and  $Y_R$  which is the background absorption signal referred to above. Simultaneous solution of above equations yield:

$$X_R + \frac{(A_2 - A_1)}{(B_1 - B_2)} \quad (\text{acid and base reagent impurities})$$

$$Y_R = A_1 - B_1 \frac{(A_1 - A_2)}{(B_1 - B_2)} \quad (\text{background absorption})$$

The values of  $X_R$  and  $Y_R$  are analogous to the original sample concentration and the blank contribution determined by Brewer et al (1969).

It is now possible to formulate a single expression for the calibration of the individual extraction preconcentrated samples. Combining the two extraction results in Equation 1:

$$Y_1 = A_1 + B_1 X \quad (\text{1st extraction})$$

$$Y_2 = A_2 + B_2 X \quad (\text{2nd extraction})$$

---


$$Y_1 + Y_2 = A_1 + A_2 + X (B_1 + B_2) \quad (1)$$

Also, subtracting background absorption from the blank absorption signal yields the absorption due to acid and base contamination ( $A_1 - Y_R = -X_R B_1$  and  $A_2 - Y_R = -X_R B_2$ ). Combining these latter two equations gives Equation 2.

$$2 Y_R = (A_1 + A_2) + X_R (B_1 + B_2) \quad (2)$$

Subtracting Equation 2 from Equation 1 results in Equation 3, which may be used for the calibration of the metal concentration recovered from aqueous samples by two successive chelation solvent extractions.

$$Y_1 + Y_2 = 2 Y_R = (X - X_R) (B_1 + B_2)$$

Thus 
$$X = \frac{Y_1 + Y_2 - 2 Y_R}{B_1 + B_2} + X_R \quad (3)$$

When applying this equation in sample calibration, the term  $Y_R$  will compensate for the instrumental background absorption. But to account for the contaminant metal introduced by the acid-base adjustment the value for  $X_R$  must be included. When the sample is chelated and extracted at its natural pH,  $X_R = 0$ .

Statistical Information: The detection limit and extraction efficiency for each metal are given in Table 1. Information about precision and affects of storage time are given in Winters, et al. (1975).

DISCUSSION: Many laboratories using similar chelation solvent extraction and atomic absorption analytical methods cannot agree on trace metal concentrations in marine aqueous intercalibration samples. Winters et al. (1976) noted that if identical samples are analyzed and if there are no instrumental errors, the observed analytical variations may be caused by improperly controlled variables in the preconcentration procedure.

Competition for the trace metals between natural ligands and the chelating reagent is not fully appreciated by many analysts. Labile or active concentrations of trace elements (such as Al, Cd, Co, Fe, Mn, Pb and Zn) occurring in natural aqueous media, are dependent on the hydroxyl ion concentration (Winters, et al., 1975). An extreme example of this hydroxyl ion dependency is apparent for iron. Only a small fraction of labile iron can be present in aqueous solutions at the natural pH of marine waters (Winters, et al., 1976). It was also noted by these authors that chelation of the total trace metal concentrations requires dissociation at low pH ( $\leq 2$ ). Raising the sample pH prior to the chelating ligand addition can result in partial trace metal hydrolysis, and the measurement of an erroneous concentration. If the sample is

chelated and extracted at its natural pH, only labile metal is recovered.

SPECIAL PROBLEMS AND SUGGESTIONS: The manganese chelate complexes are unstable in the ketone and must be analyzed as soon as possible following the extraction. The excess addition of chelating reagent is to shift the extraction process to the complex form thereby retarding the reverse process that occurs when water remains in the solvent phase.

REFERENCES: Brewer, P.G., Spencer, D.W. and Smith, C.L., 1969. Determination of trace metals in sea water by atomic absorption spectrophotometry.

Amer. Soc. for Testing and Materials. Spec. Tech. Publ. 443: 70-77.

Winters, G.V., Buckley, D.E. and Cranston, R.E., 1975. A method of evaluating labile trace metal concentrations in natural waters. Bedford Institute of Oceanography Report Series, BI-R-75-19, unpublished report.

Winters, G.V. and Perkins, C.L., 1976. Dependence of labile iron in aqueous solution on total iron, storage pH and storage time. Canadian Journal of Spectroscopy, Vol. 21, No. 2.

## ELUTRIATE WATER ANALYSIS

ABSTRACT: This test is designed to show what effects sediments that are resuspended by dredging processes will have on the surrounding water. A suspension of sediment in natural water is made and the trace metal content (Cd, Cu, Zn, Pb, Mn) in the water is analyzed by techniques previously described in the trace metal in sea water analysis section.

EQUIPMENT: Filtering apparatus and filters (0.45  $\mu$ m Millipore)  
Filtered air mixer  
Bel-Art bottles (or equivalent)  
Equipment needed for trace metal in sea water analysis

REAGENTS: Nitric acid  
Distilled water (18 mega ohms resistivity)  
Reagents needed for trace metal analysis

STANDARDS: Standards are made as previously described in the trace metal in sea water analysis section.

### PROCEDURE:

Equipment Preparation: The glassware and the Bel-Art bottles are cleaned using nitric acid followed by three separate rinses of distilled water. The Bel-Art bottles are cleaned and left standing filled with distilled water for as long as possible before use (the bottles used in this experiment were soaked for one year). The spectrophotometer is zeroed on methyl isobutyl ketone which is aspirated between samples.

The 0.45 micrometer filters are soaked in three changes of distilled water before their use.

An elutriate water blank is run in the spectrophotometer and the value is subtracted from the standard and sample results. The compressed air used in aerator is first passed through an in line dust filter and a deionized water scrubber before entering the sample container.

Sample Preparation: Water samples taken from the study area, are suction-filtered through the membrane filters into an Erlenmeyer flask. A portion of the filtrate is set aside for extraction and analysis (to give a before reaction reading), while the remainder is used in the elutriate test. The sediment samples are subsampled. One portion is homogenized using a stainless steel spatula. The other is weighed, dried at 50°C for 24 hours and reweighed so that percentage water content may be calculated. The wet sediment was added to the composite water on a volumetric ratio of 1:19 (950 ml water plus 50 ml wet sediment) so that the wet sediment would bulk the composite water to exactly 1 l. This is transferred to 2 l. Bel-Art bottles and the samples are then mixed by aeration for 30 minutes. They are allowed to stand for 1 hour. They are then decanted through the pre-rinsed filtration apparatus. Duplicate portions of this "standard elutriate" and of the unreacted water samples are extracted using the technique as described in the Trace Element Analysis. The difference between the elutriated water and the unreacted water shows the effect of the sediments.

Analysis: This is as previously described.

Statistical Information: All data is subjected to a least squares regression analysis with plotting. Additional analytical information is given in the previous section.

REFERENCES: Keeley, J.W. and Engler, R.M. 1974. Discussion of regulatory criterion for ocean disposal of dredged material. Elutriate test rationale and implementation guidelines: U.S. Army Engineers Waterways Experiment Station, Office of Dredged Materials Research, Miscellaneous Paper D-74-14, Vicksburg, Mississippi.

Lee, G.F., Piwoni, M.P., Lopez, J.M., Mariani, G.M., Richardson, J.S., Homer, D.H. and Saleh, F., 1975. Research studies on the development of

dredged material disposal criterion. U.S. Army Engineers Waterways Experiment Station, Office of Dredged Materials Research, Contract Report D-75-4, Vicksburg, Mississippi.

Winters, G.V., 1976. Elutriate test of Miramichi Channel sediments. Unpublished manuscript, 8 pp.

## QUANTITATIVE DETERMINATION OF SUSPENDED SEDIMENT

ABSTRACT: A filtration apparatus is used to determine the concentrations of suspended sediment in water of 0.01 mg/l.

EQUIPMENT: Filtration apparatus and membrane filters (Nucleopore 0.4  $\mu\text{m}$  pore size).

Polonium anti-static brush

Balance sensitive to 0.00001 g

Petri dishes

REAGENTS: Methanol

Deionized distilled water (18 ohms per cm resistivity)

### PROCEDURE;

Equipment Preparation: The filtration apparatus is equipped with a drying tube to protect the pump. Static is removed from the filters by brushing them with the polonium brush. They are weighed to the nearest 0.00001 g and stored in covered Petri dishes. Methanol is placed on the filtering cone before each filter is applied. The filters are wetted with about 50 ml of methanol. The suction apparatus is run to remove the methanol.

Sample Preparation: If only part of the sample volume is to be used for suspended sediment analysis, the sample is split by pouring into a funnel with a "Y" joint at the base. This gives representative samples. Before filtration, the volume of the sample is measured in a graduated cylinder.

Analysis: The agitated sample is carefully poured into the filtration unit. The filtrate is sucked into the collection flask and the sides of the containers on top of the apparatus are washed down with distilled water. After filtration is complete, the filters are placed in the Petri dishes with the covers slightly open so that they may be dried at 50°C for 24 hours. The filters are reweighed and the resultant difference noted is divided by the volume of the sample to





# Organic Matter Extractions and Characterizations

Wet sediment  
↓ Dry and pulverize  
Sediment Powder

Distill with 90% benzene and 10% methanol mixture for 18 hours in Column I.

↓  
Benzene-methanol extract

↓  
Extracted sediment

Redistill to reduce volume. Add pentane. Transfer to Column II, Add pentane.

↓  
Pentane soluble extract

↓  
Asphaltene in Column II

↓ Dry and weigh

↓  
Bitumen

↓ Add alternate additions of benzene and methanol

↓ Redissolve in pentane. Pour into Column III. Add pentane.

↓  
Eluted Column II

↓  
Benzene and methanol extract

↓ Dry and weigh  
↓  
Asphaltenes

↓  
Pentane extract

↓  
Pentane-eluted Column III

↓ Dry and weigh

↓ Add benzene

↓  
Benzene extract

↓  
Benzene-eluted Column III

↓ Dry and weigh  
↓  
Aromatics

↓ Add methanol

↓  
Methanol extract

↓  
Methanol-eluted Column III

↓ Dry and weigh

↓  
NSO compounds

↓  
Saturates

yield the sediment concentration in mg/l.

Statistical Information: The detection limit is 0.01 mg/l. The filtering efficiency, as measured by filtering latex beads from 0.31 to 2.0  $\mu\text{m}$  diameter, is 96% with a standard deviation of 3%. For Kaolinite with diameters less than 4  $\mu\text{m}$  the efficiency is 92% with a 1% standard deviation. For more detail, and for information about other filters and filtration times, consult Cranston and Buckley (1972).

DISCUSSION: Six filtrations are done at a time. When the "Y" split is used all the material to be split is held in the funnel before the ends of the "Y" are opened. This gives most representative samples.

SPECIAL PROBLEMS AND SUGGESTIONS: Blanks may be run using distilled water to check the system. All filters must be handled by tweezers and checked for holes. Holes are indicated by unusually fast filtration. Different results may be obtained when different types of filters are used (Cranston and Buckley, 1972).

REFERENCES: Cranston, R.E. and Buckley, D.E., 1972. Bedford Institute of Oceanography Report, BI-R-72-7, 14 p.

## QUALITATIVE DETERMINATION OF SUSPENDED SEDIMENT

ABSTRACT: The scanning electron microscope is used for qualitative determination of the composition of sediments suspended in water. This procedure allows estimation of the clay mineral to biogenic material ratio in the sediments; identification of the types of each present can also be made.

EQUIPMENT: Scanning Electron Microscope with coating unit

### PROCEDURE:

Equipment Preparation: The equipment presentation is as described in manuals for SEM and coating unit.

Sample Preparation: The sample suspension is filtered as described in "Quantitative Determination of Suspended Sediments". The resulting dried filter containing the sediments is cut out to fit the circular specimen stubs. The filter is adhered to the stub with either double sided tape or silver conducting paint. The filters are then coated to create a conductive surface as required for the SEM.

Analysis: The samples are scanned and photographed as described in the SEM manual.

DISCUSSION: The photographs resulting from SEM scanning are examined and compared with photographs of samples of known composition. This enables identification of clay minerals, and biogenic material, including foraminifera, that are present in the sediment sample. Because the filter and sediment have a rough surface, an optical system would not be able to focus over the complete surface, as the SEM can.

Because this an optical method, the results indicate volume percentages rather than weight percentages.

REFERENCES: Walker, D.A. and Buckley, D.E., 1969. Some techniques and Applications of Scanning Electron Microscopy in the fields of Marine Science. Maritime Sediments, Vol. 5, No. 3, pp. 113-118.

## SEDIMENT SIZE ANALYSIS

ABSTRACT: Grain size distribution of unconsolidated sediments is determined by a sieve analysis for sand and a pipet analysis for silt and clay.

EQUIPMENT: Stainless steel sieves  
R-0-Tap sieve shaker  
Sieve brush  
Balance (0.001 g)  
Drying oven  
Settling cylinders (1000 ml)  
Stainless steel riffle sample splitter  
Tumbling apparatus or mechanical mixer

Optional: Ultrasonic bath  
Constant temperature water bath  
Centrifuge

REAGENTS: Hydrogen peroxide  
Hydrochloric acid (1N)  
A dispersing agent (EMG used Calgon which is  $1.1 \text{ Na}_2\text{O} \cdot 1\text{P}_2\text{O}_5$ )  
Distilled water

### PROCEDURE:

Equipment Preparation: Tare all empty weighing beakers.

Sample Preparation: To remove organic material in the sediment samples, they are treated with hydrogen peroxide, a 10 percent solution, while the sample is heated in a water bath. The amount of peroxide added and the temperature maintained by the bath can be varied; reaction is allowed to continue to completion. When the reaction has ceased, the sample is washed two or three times with distilled water. Removal of organic material may be desirable because organic material can bind together fine material into aggregates, which have a large size than the material itself. If carbonates are to be removed, the sediment is then treated with 1 N hydrochloric acid in a treated water bath following the same operation as the hydrogen peroxide conditioning. These steps are performed when necessary otherwise the samples are simply distilled water rinsed.

The sand samples are washed with distilled water and they are placed in the drying oven at 45°C until they are completely dry. A mechanical sample splitter or the coning and quartering method is used to split the sample to get the desired weight. The necessary weights of sample to be used in order to obtain statistically valid results are as follows: fine gravel - 500 g; coarse sand - 200 g; medium sand - 100 g; and fine sand - 30 g to 70 g.

If the sample contains abundant gravel the gravel fraction (>2 mm) is removed by sieving, and the sand fraction is split to obtain the amount desired for sieving. The "splitting factor" is recorded so that weight percentages of sand and gravel can be calculated. Sieving analysis is finally used to sort the sand fractions.

Mixed mud and sand or plain mud samples are mixed until pliable and then they are split by the coning and quartering method. The split is made to yield from 10 g to 30 g of mud for the pipet analysis.

The sample is disaggregated with distilled water in a tumbling apparatus or mechanical mixer. The mud is separated from the sand by wet sieving with distilled water through a 0.063 mm sieve. The sand fraction greater than 0.063 mm is oven dried at 45°C and retained for sieve analysis. The suspension obtained from the wet sieve is transferred to a 1000 ml settling cylinder. Twenty ml of dispersal agent (50 g Calgon/1000 ml distilled water) is added to the suspension. The concentration of the solution is a sediment-character dependent factor. The suspension is stirred and left to stand for several hours to determine whether flocculation has occurred. The pan fraction of the sand component of the sample that was subjected to the dry sieve analysis can be added to the settling cylinder if the suspension has been effectively dispersed. The volume is bulked to 1000 ml with distilled water. The pipet analysis is now performed.

Analysis: The sieve analysis is started by weighing the samples to the nearest

0.01 g. The Rotap sieve shaker uses stainless steel sieves ranging from  $-5\phi$  to  $4\phi$  (read phi) to sort the sample for 15 minutes. Different  $\phi$  intervals can be used,  $\frac{1}{4}\phi$ ,  $\frac{1}{2}\phi$ ,  $1\phi$ , depending on the desired results. Each sieve fraction is weighed to the nearest 0.01 g. The pan fraction remaining from this sieving is added to the settling cylinder if a pipet analysis is required. If no pipet analysis is to follow, the pan fraction is also weighed to 0.01 g.

For a pipet analysis the contents of the settling cylinder are stirred for 45 seconds and 20 seconds later a pipet is inserted to a depth of 20 cm and filled to get a collection of  $4\phi$  particles.  $5\phi$  particles are collected at one minute, fifty-six seconds at 10 cm depth.  $6\phi$  particles are collected at 7 minutes, forty-four seconds at 10 cm depth. At 31 minutes and 10 cm depth,  $7\phi$  particles are siphoned.  $8\phi$  particles are collected at 2 hours, 3 minutes at 10 cm depth and  $9\phi$  particles are collected at 4 hours, 6 minutes at 5 cm depth.

Each  $\phi$  subsample is dried at  $75-80^{\circ}\text{C}$  in the oven, in the pretared beakers. The subsamples are weighed to the nearest 0.001 g and the weight of the added volume of dispersing agent is calculated and subtracted from the total weight. The resultant subsample weight is subtracted from the weight of the immediately preceding subsample. This gives the amount of material in each size grade. Multiplication of this weight by 50 corrects for the volume difference between the 20 ml pipet and the 1 l settling column, and so gives the total amount of material in each size fraction. Pipet analyses can be performed using smaller ( $\frac{1}{4}\phi$  or  $\frac{1}{2}\phi$ ) or greater ( $2\phi$ ,  $4\phi$ ) intervals; for more information consult the references which follow.

Statistical Information: The weight percentage of the total sample for each size interval is calculated. Various computer programs are used for this purpose and for performing statistical analysis on the grain size data. For details on

statistical and graphic presentations of grain size data, the references should be consulted.

DISCUSSION: The size and number of additions and washes performed on the samples are dependent on the type of sediments being handled. Although a basic procedure is described, it must not be considered inflexible. Adjustments must be made as necessary to attain the best results (e.g. weight of sample analyzed).

The chemical composition of the sediments used in size analysis is not a constraint to be concerned with. Various different dispersing agents can be used to attain equally good results.

Dust, soluble salts and other cementing agents are removed by the distilled water washes of these sediments. Most special problems can be solved by established techniques described in the references.

REFERENCES: Carver, R.E. (editor), 1971. Procedures in sedimentary petrology.

Wiley Interscience, New York, 653 pp.

Folk, R.L., 1966. A review of grain size parameters. *Sedimentology*, 6: 73-93.

\_\_\_\_\_, 1968. *Petrology of sedimentary rocks*. Hemphill's, Austin, Texas, 170 pp.

Krumbein, W.C. and Pettijohn, F.J., 1938. *Manual of sedimentary petrography*. Appleton-Century-Crafts, Inc., New York, 549 pp.



# Wet sediments

If organic material and carbonates are to remain in sample, rinse three times with distilled water.

If organic material is to be removed before analysis, treat with hydrogen peroxide. Rinse three times with distilled water.

Sample

Organic residue

If carbonate-free samples are desired, treat with hydrochloric acid and rinse three times with distilled water.

Dust, soluble salts etc.

Cleaned, wet samples

Carbonate residue

Pure sands

Heterogeneous

Pure muds

Wet sieve

Mix until pliable

Course (>63 mm.)

Muds (<63 mm.)

Dry then dry sieve

Sands (<2 mm.)

Gravel (>2 mm.)

Dry then dry sieve

Make suspension  
Add dispersing agent. Stir.  
Let stand. If no flocculation occurs, do pipet analysis

Size fractionated sands. Weigh.

Pan sample. Small amount of mud.

Size fractionated muds. Dry and weigh.

# Sediment Textures

## Grain Size Scales for Sediments - from

Folk, R.L., 1968. Petrology of Sedimentary Rocks.  
Hemphill's, Austin, Texas, 170 pp.

U.S. Standard Sieve Mesh #	Millimeters	Microns	Phi ( $\phi$ )	Wentworth Size Class	
	4096		-12		GRAVEL
	1024		-10	Boulder (-8 to -12 $\phi$ )	
Use _____	256		-8	Cobble (-6 to -8 $\phi$ )	
wire _____	64		-6	Pebble (-2 to -6 $\phi$ )	
squares _____	16		-4		
5 _____	4		-2		
6 _____	3.36		-1.75		
7 _____	2.83		-1.5	Granule	
8 _____	2.38		-1.25		
10 _____	2.00		-1.0		
12 _____	1.68		-0.75		SAND
14 _____	1.41		-0.5	Very coarse sand	
16 _____	1.19		-0.25		
18 _____	1.00		0.0		
20 _____	0.84		0.25	Coarse sand	
25 _____	0.71		0.5		
30 _____	0.59		0.75		
35 _____	1/2	500	1.0		
40 _____	0.42	420	1.25		
45 _____	0.35	350	1.5	Medium sand	
50 _____	0.30	300	1.75		
60 _____	1/4	250	2.0		
70 _____	0.210	210	2.25		
80 _____	0.177	177	2.5	Fine sand	
100 _____	0.149	149	2.75		
120 _____	1/8	125	3.0		
140 _____	0.105	105	3.25		
170 _____	0.088	88	3.5	Very fine sand	
200 _____	0.074	74	3.75		
230 _____	1/16	62.5	4.0		
270 _____	0.053	53	4.25		MUD
325 _____	0.044	44	4.5	Coarse silt	
	0.037	37	4.75		
	1/32	31	5.0		
	1/64	15.6	6.0	Medium silt	
Analyzed _____	1/128	7.8	7.0	Fine silt	
by _____	1/256	3.9	8.0	Very fine silt	
	0.0020	2.0	9.0		
Pipette _____	0.00098	0.98	10.0	Clay	
	0.00049	0.49	11.0		
or _____	0.00024	0.24	12.0		
	0.00012	0.12	13.0		
Hydrometer _____	0.00006	0.06	14.0		

## TOTAL BULK MAJOR ELEMENTS

ABSTRACT: Sediments are subjected to a total decomposition technique, using strong acids which allows analysis of 18 elements by Atomic Absorption spectrophotometry. The main advantage of this technique over the other existing techniques is its greater speed of operation, while its precision and accuracy are comparable to the others. Detection limits allow analysis of many trace metals (Co, Cr, Cu, Li, Ni, Pb, Sr, V, and Zn) along with the major elements (Al, Ca, Fe, K, Mg, Mn, Nr, Si and Ti) from a single decomposition. Detection limits accuracy, and precision (as of 1970); Improved Instrumentation has improved all of these) are shown in Tables II-IV.

EQUIPMENT: Atomic absorption spectrophotometer and recorder  
Teflon bombs  
Heating unit  
Polypropylene bottles  
Glass volumetric flask

REAGENTS: Hydrofluoric acid (HF)  
Hydrochloric acid (HCl)  
Nitric acid (HNO<sub>3</sub>)  
Boric acid (H<sub>3</sub>BO<sub>3</sub>)  
Deionized distilled water

The standards are made using high purity metals or salts as noted in Table I of Buckley and Cranston (1971), which is included here. They are originally prepared in 1 litre stock to give a cation concentration of 1.000 µg/ml each and they are then combined to give the concentrations desired in the mixed standard (standard A in Table I). The purpose of making up the mixed standard is to match the matrix of the standard to that of the samples, which compensates for interelement interference. A 6% v/v hydrofluoric acid, 5.6% w/v boric acid and 1% v/v aqua regia content is maintained throughout in the additional dilutions of the first standard combination (1:2, 1:10, 1:20). This solution

is also used as the balance solution.

PROCEDURE:

Equipment Preparation: The teflon bombs are acid cleaned and rinsed with deionized distilled water three times, as are the polypropylene bottles and the volumetric flasks. The spectrophotometer and recorder are set up in accordance with the manufacturer's manual, with the exceptions noted in Table II.

Sample Preparation: 0.100 g samples of sediment are weighed out into the teflon bombs. They are then wetted with 1 ml aqua regia (3 parts concentrated HCl mixed with 1 part concentrate  $\text{HNO}_3$ ) and 6 ml of concentrated HF. The bombs are sealed and heated at  $100^\circ\text{C}$  for 30 min. Following a cooling period, they are washed into 125 ml polypropylene bottles which contain 5.6 g of  $\text{H}_3\text{BO}_3$  and 20 ml deionized distilled water. The sample solutions are thoroughly shaken and then transferred to glass volumetrics and brought to 100 ml with deionized distilled water. For storage, the samples are returned to the polypropylene bottles.

Analysis: The spectrophotometer is zeroed by aspirating deionized distilled water.

The prepared samples are aspirated into the spectrophotometer's flame and the results are chart recorded.

The standards are used to calibrate the machine before the samples are analyzed and standards are reanalyzed intermittently during the sample analysis.

Statistical Information: Values for precision and detection limit are given in Tables II and III, from Buckley and Cranston (1971). Accuracy is indicated in Tables III and IV in this reference by analysis of standard rocks. These tables are reproduced values.

A segmented curve is calculated using the derivative between each pair of

standards. The sample concentrations are interpolated from within the ranges. Computer plotting removes biases. This is further discussed in Buckley and Cranston (1971).

DISCUSSION: This technique and others that are similar, are thoroughly discussed in Buckley and Cranston (1971).

Deionized distilled water is aspirated between samples as the blank solution proved to be too destructive on the equipment for continuous use.

As no fluxes are used with teflon bomb technique, all alkali and alkaline earth elements could be analyzed. The sealed bomb reduces the possibility of volatilization loss of Si, Al, V and Ti.

Only one sample solution and 4-6 standards are needed using this technique.

To decompose and dilute 20 samples and make the necessary standards takes about one day.

PROBLEMS AND SUGGESTIONS: There is little glassware contamination in this test.

Coefficients of variations on the plotted results often vary due to different "noise" levels for the elements in the apparatus and the minute concentrations of some of the components.

Some clay samples require 100°C treating for 60 minutes (rather than 30) in the teflon bombs in order to be totally digested.

The treating should be done in a closed area (fume hood) to protect against acid sprays from explosions.

REFERENCE: Buckley, D.E. and Cranston, R.E. Chemical Geology (1971), Vol. 7, pp. 273-284.

TABLE I  
 Elemental standards

Major elements	Al	Ca	Fe	K	Mg	Mn	Na	Si	Ti
Source	metal	CaCO <sub>3</sub>	metal	KCl	metal	metal	NaCl	SiO <sub>2</sub>	TiO <sub>2</sub>
Solvent	HCl	HCl	HCl	water	HCl	HCl	water	HF <sup>1</sup>	HF <sup>1,2</sup>
Std. A (ug/ml.)	100	100	100	50	50	2	40	350	20

Minor elements	Co	Cr	Cu	Li	Ni	Pb	Sr	V	Zn
Source	metal	K <sub>2</sub> CrO <sub>4</sub>	metal	LiCl	metal	metal	Sr(NO <sub>3</sub> ) <sub>2</sub>	V <sub>2</sub> O <sub>5</sub>	metal
Solvent	HNO <sub>3</sub>	water	HNO <sub>3</sub>	water	HNO <sub>3</sub>	HNO <sub>3</sub>	water	HCl	HCl
Std. A (ug/ml.)	0.2	0.5	0.2	0.1	0.3	0.2	1.0	0.5	0.2

<sup>1</sup>Decomposition carried out in teflon bomb.

TABLE II  
 Analytical conditions for atomic absorption spectroscopy

Major elements	Al	Ca	Fe	K	Mg	Mn	Na	Si	Ti
Upper limit elemental conc. in rock	15%	10%	10%	5%	5%	0.3%	4%	35%	3%
Upper limit oxide conc. in rock	28%	14%	14%	6%	8%	0.4%	5%	75%	5%
Sensitivity (ug/ml/1%abs)	1.2	1.3	4.0	1.5	0.6	0.06	0.5	4.0	2.0
Burner type <sup>1</sup>	N	N	5 cm	5 cm	N	B	5 cm	N	N
Burner position <sup>2</sup>	//	+	+	+	+	//	+	//	//
Recorder exp.	× 1	× 1	× 3	× 3	× 1	× 3	× 1	× 1	× 10

Minor elements	Co	Cr	Cu	Li	Ni	Pb	Sr	V	Zn
Lower limit conc. in rock (p.p.m.)	20	20	10	10	20	50	100	100	20
Sensitivity (ug/ml/1%abs)	0.15	0.20	0.07	0.05	0.15	0.50	0.12	1.0	0.20
Burner type <sup>1</sup>	B	B	B	B	B	B	N	N	B
Burner position <sup>2</sup>	//	//	//	//	//	//	//	//	//
Recorder exp.	× 30	× 30	× 30	× 30	× 30	× 30	× 10	× 30	× 10

<sup>1</sup>5 cm = short path air-acetylene burner; N = nitrous oxide-acetylene burner; and B = Boling (3 slot) burner.

<sup>2</sup>// = burner parallel to light path; and + = burner perpendicular to light path.

TABLE III

Results for replicate analyses

Major elements (%)	Al	Ca	Fe	K	Mg	Mn	Na	Si	Ti
<b>W-1</b>									
Present <sup>1</sup>	7.97	7.83	7.78	0.531	3.99	0.132	1.54	24.5	0.64
Found	8.17	7.66	7.72	0.540	4.20	0.131	1.56	24.6	0.63
Std. dev.	0.29	0.77	0.27	0.02	0.29	0.005	0.114	1.2	0.03
Coeff. var.	3.5	10.0	3.5	3.7	6.9	3.8	7.3	4.8	4.8
% difference	+2.5	-2.2	-0.8	+1.9	+2.8	-0.8	+1.3	+0.1	-1.6
<b>Illite 35</b>									
Found	9.85	0.92	3.89	3.64	1.37	0.0275	0.41	25.5	0.50
Std. dev.	0.25	0.07	0.13	0.10	0.07	0.0014	0.03	1.6	0.035
Coeff. var.	2.5	7.6	3.3	2.7	5.1	5.1	7.3	6.3	7.0
Minor elements (p.p.m.)	Co	Cr	Cu	Li	Ni	Pb	Sr	V	Zn
<b>W-1</b>									
Conc. range <sup>1</sup>	35-55	90-160	80-150	10-12	55-88	5-10	150-300	120-320	20-95
Found	68	128	105	14	81	<50	167	249	88
Std. dev.	18	8	17	3	12	-	19	34	8
Coeff. var.	26	6	16	21	15	-	11	14	9
<b>Illite 35</b>									
Found	45	113	60	48	80	53	118	178	86
Std. dev.	12	18	15	4	17	13	16	43	13
Coeff. var.	27	16	25	8	21	24	14	24	15

<sup>1</sup>Values from Fleischer and Stevens (1962).

TABLE IV

U.S.G.S. Standard Rocks

Major elements (%)	Al	Ca	Fe	K	Mg	Mn	Na	Si	Ti
<b>AGV-1 present<sup>1</sup></b>									
found a)	9.00	3.56	4.75	2.41	0.90	0.076	3.21	27.5	0.65
b)	9.17	3.86	4.59	2.31	0.96	0.074	3.15	29.6	0.61
found b)	9.32	4.01	4.58	2.34	0.96	0.073	3.10	28.0	0.65
<b>BCR-1 present</b>									
found a)	7.22	4.97	9.44	1.39	1.98	0.136	2.46	25.4	1.34
b)	7.25	5.07	9.04	1.29	2.10	0.137	2.17	25.1	1.30
found b)	7.43	5.09	8.98	1.28	2.10	0.138	2.16	23.2	1.30
<b>GSP-1 present</b>									
found a)	8.00	1.45	3.03	4.56	0.58	0.034	2.14	31.4	0.42
b)	8.00	1.58	3.00	4.70	0.55	0.034	1.94	31.6	0.42
found b)	8.27	2.11	2.92	4.69	0.55	0.031	1.94	30.0	0.42
<b>G-2 present</b>									
found b)	8.11	1.42	1.93	3.74	0.47	0.026	3.08	32.3	0.32
found b)	8.45	1.97	1.81	3.71	0.42	0.025	3.03	30.8	0.30
<b>W-1 present<sup>2</sup></b>									
found b)	7.97	7.83	7.78	0.53	3.99	0.132	1.54	24.5	0.64
found b)	8.20	8.04	7.66	0.53	4.11	0.133	1.51	22.5	0.68
Minor elements (p.p.m.)	Co	Cr	Cu	Li	Ni	Pb	Sr	V	Zn
<b>AGV-1 range<sup>1</sup></b>									
found a)	10-30	7-45	50-83	9-14	11-31	18-48	348-1050	70-171	64-304
b)	31	20	43	10	61	<50	631	111	79
found b)	32	20	43	11	63	<50	631	101	78
<b>BCR-1 range</b>									
found a)	29-60	8-45	7-33	10-19	6-30	4-35	244-550	120-700	94-278
b)	43	47	13	12	27	<50	311	476	112
found b)	46	56	16	14	27	<50	319	476	112
<b>GSP-1 range</b>									
found a)	3-22	5-18	8-54	25-47	3-25	14-80	148-400	25-68	54-340
b)	23	59	18	40	31	62	268	111	84
found b)	24	54	19	29	31	<50	274	101	83
<b>G-2 range</b>									
found b)	2-21	5-29	2-17	26-63	2-14	15-43	235-650	26-60	42-138
found b)	20	20	16	30	20	<50	473	100	73
<b>W-1 range<sup>2</sup></b>									
found b)	35-55	90-160	80-150	10-12	55-88	5-10	180-300	120-320	20-95
found b)	55	174	120	25	63	<50	205	209	80

<sup>1</sup>Flanagan (1969).

<sup>2</sup>Fleischer and Stevens (1962).

## MERCURY ANALYSIS

ABSTRACT: A strong acid leach is used to break down the sedimentary complexes and extract the mercury in the samples. The extracts are examined by an analyzer employing a cold vapour, flameless atomic absorption spectrophotometer. A regression analysis is performed on the data, which is collected in the ppb range.

EQUIPMENT: Drying oven  
BOD bottles (300 ml)  
Cold vapour, flameless, atomic absorption, mercury analyzer and recorder

REAGENTS: Sulphuric acid (36 N)  
Nitric acid (16 N)  
Tin chloride (1 N  $\text{SnCl}_2$ )  
Deionized, distilled water (18 mega ohms per cm resistivity)

STANDARDS: A stock solution of 1000 ppm of mercury is made by dissolving mercuric chloride in concentrated nitric acid and distilled water to give a pH 1 solution. From this an intermediate 1 ppm solution is made by diluting the stock solution with deionized distilled water.

### PROCEDURE:

Equipment Preparation: The BOD bottles, when new, are preconditioned by cleaning with nitric acid, rinsing with deionized distilled water three times and baking at  $250^{\circ}\text{C}$  for 24 hours before use. Following the analysis, the BOD bottles are well rinsed with deionized distilled water and then they are filled with deionized distilled water until future use.

The plastic cell in the analyzer is replaced with a quartz glass cell of the identical size and shape, for better transmission and detection limit. The instrument is zeroed on air. This blank is subtracted from the standard and sample values by adjusting the recorder output. A calibration curve is established by analyzing various volumes of the 1  $\mu\text{g}/\text{ml}$  intermediate standard solution. A reagent container control blank is run to check for the presence



of Hg signal enhancement within the system.

Sample Preparation and Analysis: Deionized distilled water is used to remove the interstitial salts if the results are to show only the metal bound in the sediment.

The samples are dried at 50°C for 24 hours. The samples are lightly pulverized and then are weighed out in 50 mg portions into the BOD bottles. Additions of 20 ml of sulphuric acid and 10 ml of nitric acid are made and the BOD bottles are treated at 60°C for one hour. The samples are bulked to 200 ml with deionized distilled water and cooled to 20°C. The mercury content is reduced to the elemental form by a 10 ml addition of tin chloride (1 N SnCl<sub>2</sub>) which causes volatilization of the mercury. Aeration is begun immediately and the mercury vapour is flushed into the quartz cell and the absorbance is measured on the chart recorder.

Statistical Information: The results of the recorder are plotted on a linear regression against the standards Hg content. The micrograms of Hg in a 50 milligram sample are defined by this plot. The detection limit of 2 ppb and a coefficient of variation of 5% have been found by this method on 10 replicate samples in the 50 to 1000 ppb concentration range.

DISCUSSION: Wet, unwashed samples are altered the least (reducing experimental error) but they also yield poorer reproducibility due to evaporation during the weighing step. The samples are washed for Sediment Size Fractionation and Bulk Analysis comparability.

The spectrophotometer adaptation as described by Hatch and Ott, 1968, was previously used but it has proven to be disadvantageous for several reasons: it was expensive to maintain and set up; the longer analytical time requirement due to the size of the vapourization tube gave "memory" effects in the readout;

it tied up valuable spectrophotometer time and more laboratory space and it was not portable for field examinations. The recorder is used with the analyzer because the voltmeter reproducibility is better and a permanent record is obtained.

DISCUSSION: The "cooking" of the BOD bottles is to anneal the glass surface thereby destroying possible contaminants and activation sites.

SPECIAL PROBLEMS AND SUGGESTIONS: High quality sulphuric acid is used to ensure that it is mercury free. Fitzgerald, Gordon and Cranston, 1974, reported that even at a pH 1 storage up to 57% of the Hg could be lost if the samples are stored for 10 days or more. In light of this, the 1 ppm standard solution should be made up every two weeks.

In order to maintain the Beer's Law relationship, the absolute Hg level is not permitted to exceed 0.2  $\mu\text{g}$  in sample or standard injections. If it is believed that this level will be exceeded, smaller samples must be used or the samples can be diluted before injecting. The volatile mercury may be lost to the atmosphere when it is produced by the fast preparation reaction, hence, the aeration should begin immediately following the acid treatment.

REFERENCES: Cranston, R.A. and Buckley, D.E., 1972. Mercury pathways in a river and estuary. Environmental Science and Technology, 6: 274-278.

Fitzgerald, R.A., Gordon, D.C., Jr. and Cranston, R.E., 1974. Total mercury in seawater in the northwest Atlantic Ocean. Deep Sea Research, 21: 139-144.

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

## WEAK ACID LEACHABLE METALS

ABSTRACT: This method employs acetic acid to remove from sediments only free or loosely bound metals, or metals associated with Calcium Carbonate (Fe, Ca, Mn, Cu and Zn). The extracts are examined by atomic absorption spectrophotometry with good precision in the ppm range.

EQUIPMENT: Balance (0.001 g)

Drying oven

Atomic absorption spectrophotometer

REAGENTS: Acetic acid (20%)

Deionized distilled water (18 mega ohms per cm. resistivity)

STANDARDS: Standards are made from refrigerated stock solutions of 1000 ppm pure metal in acid. The diluted stock solutions are combined into a unit standard containing 200 ppm Ca, 100 ppm Fe, 20 ppm Mn, 2 ppm each of Zn, Pb and Cu in 20% acetic acid. Additional dilutions (which must maintain the consistency between the standard and sample matrices) are commonly made 1:2, 1:10 and 1:20 with acetic acid or deionized distilled water.

PROCEDURE:

Equipment Preparation: The spectrophotometer is operated in accordance with the manufacturer's manual.

Sample Preparation: The wet sediment samples are dried at 50°C for 24 hours. After being lightly pulverized, 1.000 g aliquots are weighed out and added to 50 ml beakers along with 20 ml of 25% acetic acid. After reacting for 24 hours, the resultant leachate is decanted into a 25 ml volumetric flask. Deionized distilled water is used to bulk the leachate to the mark. The aqueous sample is now stored; the pH is approximately 2. Before the Ca and Fe analyses, 2.5 ml portions are put into test tubes and bulked 1:10 with deionized distilled water.

Analysis: The spectrophotometer is zeroed on deionized distilled water and the recorder output is calibrated by the standards' results. The standards are run intermittantly with the samples to check for machine drift. A blank containing acetic acid is run and its value is subtracted from the results of both the samples and the standards. Deionized distilled water is used throughout as the baseline aspirate.

Statistical Information: Analytical detection limits and precision are given in Table R-2 in Cranston, Fitzgerald and Winters (1974). This table is reproduced below.

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Table R-2 - Analytical Precision and Detection Limits for  
Analyses of Sediment Samples

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<u>Measurement</u>	<u>Units</u>	<u>Precision (%)</u>	<u>Detection Limit</u>
Fe	ppm	5	10
Mn	"	5	5
Ca	"	10	5
Cu	"	15	0.1
Zn	"	10	0.5

---

DISCUSSION: In contrast to the total decomposition of the metallic complexes in the sediments by strong acid digestion, as is done in a Total Bulk Analysis, this technique leaves the sediments very much intact. Free or loosely bound components and those associated with calcium carbonate are the only forms removed. The measurement of their concentration is performed to give an indication of what is readily available to the natural environment.

SPECIAL PROBLEMS AND SUGGESTIONS: The analysis of samples should begin as soon as possible following the leaching step. If the samples are to be stored, they should be refrigerated to retard their breakdown.

REFERENCES: Buckler, J.D., 1973. Environmental geochemistry of the Cobequid  
of Canso and Chedabucto Basins at Hawkesbury, Nova Scotia. Bedford Institute  
of Oceanography, Field Report No. 73-022, p. 26.

Chester, R. and Hughes, M.J., 1967. A new technique for  
the separation of ferro-manganese minerals, carbonates, and adsorbed  
trace elements from pelagic sediments. Chem. Geol. 1: 1-17.

Willey, J.D., 1974. Geochemistry and environmental implications  
of the surficial sediments from Placentia Bay, Newfoundland. Canadian  
J. of Earth Sciences, 13: In press.

## REDUCABLE METALS

ABSTRACT: A weak acid and reducing agent combination is used to selectively extract the hydrogenous and/or biogenous fraction of the total trace element content (Fe, Mn, Ca, Zn, Pb and Cu) incorporated in marine sediments. The quantitative analysis by spectrophotometry is good enough to yield precision in the ppm range.

EQUIPMENT: Atomic Absorption spectrophotometer and recorder  
Drying oven  
Balance (0.001 g)

REAGENTS: Acetic acid  
Hydroxylamine hydrochloride ( $\text{NH}_2\text{OH}\cdot\text{HCl}$ )  
Deionized distilled water (18 mega ohms per cm resistivity)

The leaching solution is made by mixing 150 ml of 25%  $\text{NH}_2\text{OH}\cdot\text{HCl}$  (w/v in deionized distilled water) with 350 ml of 35% acetic acid. This gives a solution which is 1 M  $\text{NH}_2\text{OH}\cdot\text{HCl}$  and 25% acetic acid.

STANDARDS: Standards are made from refrigerated stock solutions of 1000 ppm of pure metal in acid. A combined standard is made up containing 25 ppm Ca, 25 ppm Fe, 2 ppm Mn, 2 ppm Zn and 2 ppm Pb. The stock solutions are diluted with leaching solution or with distilled water in order to match the matrices of the standards with the samples.

### PROCEDURE:

Equipment Preparation: The spectrophotometer and its recorder are prepared and operated in accordance with the manufacturer's manual.

Sample Preparation: The wet sediment collections are dried at  $50^\circ\text{C}$  for 24 hours. They are gently pulverized and weighed out to 1.000 g and added to 50 ml beakers. Twenty ml of leaching solution is added to each 1.000 g sediment. After leaching for 24 hours the aqueous phase is decanted into a 25 ml volumetric. To the solid phase is added 5 ml of distilled water which is stirred in, settled

out and decanted into the volumetric flask. After bulking to 25 ml with deionized distilled water, the whole volume is allowed to stand in order to settle out any remaining residue. Finally, the aqueous phase is poured off into storage test tubes. Before the spectrophotometer analysis Zn, Ca and Fe 2.5 ml aliquots of the samples are diluted 1:10 with deionized distilled water.

Analysis: The undiluted samples (for Mn, Zn and Pb) and the diluted samples (for Ca and Fe) are each read on the spectrophotometer. Deionized distilled water is aspirated between samples. The recorder is intermittantly checked with the calibration standards between sample runs to check for machine drift. Blank solutions of 80% or 8% leaching solution (depending on the sample dilution factor) are run and these blank values are subtracted from the sample and standard readings.

Statistical Information: Precision and detection limits should be similar to those reported in the Weak Acid Leach Technique.

DISCUSSION: The Ca and Fe standards may be made in distilled water and adjusted to 8% of the leaching solution. If the standard levels are too high they can be further diluted by 1:2, 1:5 or 1:10 in pure leaching solution or by maintaining the 8% leaching solution in distilled water. The matrices of the samples and the standards must be matched with respect to the hydroxylamine and acetic acid content. The time requirements are one day for preparation and one day for spectrophotometer analysis of 25 samples for 6 elements.

SPECIAL PROBLEMS AND SUGGESTIONS: In the absence of a recorder, the spectrophotometer results are read off the digital readout and an expansion factor is used. The average of several readings is taken and the blank value is subtracted to yield the difference which can be converted to concentration. The precision of this operation is improved by increasing the time averages.

To obtain as uniform results as is possible, the leaching solution is made up in large batches and it is refrigerated between uses. If less than 1.000g sample is available, 0.500 g or 0.250 g can be weighed out instead. All additions are adjusted accordingly. Copper concentrations in many samples have been found to be very close to the detection limit, consequently this analysis is not performed routinely.

REFERENCES: Chester, R. and Hughes, M.J., 1967. A chemical technique for the separation of ferro-manganese minerals, carbonate minerals and adsorbed trace elements from pelagic sediments. Chem. Geol., 2: 249-262.

Chao, T.T., 1972. Selective dissolution of manganese oxides from soils and sediments with acidified hydroxylamine hydrochloride. Soil Sci. Soc. Amer. Proc., 36: 764-768.



## ORGANICALLY BOUND METALS

ABSTRACT: A hydrogen peroxide leaching process is used to remove metallic complexes of Fe, Mn, Ca, Zn, Cu, and Pb bound primarily with the organic constituents in sediments. Atomic absorption spectrophotometry is used to examine the extracts. The precision obtained is good in the ppm range.

EQUIPMENT: Balance (0.001 g)  
Drying oven  
Filtration system  
Atomic absorption spectrophotometer

REAGENTS: Acetic acid (20%)  
Hydrogen peroxide (10%)  
Deionized distilled water (18 mega ohms per cm resistivity)

STANDARDS: Standards are made from refrigerated stock solutions of 1000 ppm pure metal in acid. The combined standard is prepared by diluting aliquots of the 1000 ppm stock solutions. The standard should contain 100 ppm Fe, 200 ppm Ca, 20 ppm Mn, 2 ppm each of Cu, Zn and Pb in 20% acetic acid. This may be further diluted with acetic acid to 1:2, 1:10 or 1:20 depending on the requirements. The matrices of the standards must match the samples.

### PROCEDURE:

Equipment Preparation: The spectrophotometer and the recorder are set up in accordance with the manufacturer's manual.

Sample Preparation: The wet sediment samples are dried at 50°C for 24 hours. After being lightly pulverized, 1.000 g aliquots are weighed out and added to 50 ml beakers along with 20 ml of 10% hydrogen peroxide. After reacting for 24 hours, the resultant leachate is decanted into a 25 ml volumetric flask. An addition of 5 ml of glacial acetic acid is made to the volumetric flask, followed by deionized distilled water to bring the volume to 25 ml. The samples so prepared have a pH of approximately 2 and they can be stored.

Analysis: The spectrophotometer is zeroed on deionized distilled water and the recorder output is calibrated by the standards' results. The standards are run intermittently with the samples to check for machine drift. A blank containing acetic acid is run and its value is subtracted from the results of both the samples and standards. Deionized distilled water is used throughout as the baseline aspirate.

Statistical Information: Analytical detection limits and experimental precision are equivalent to those reported in the Weak Acid Leach Method because the solutions obtained after each leach are similar.

DISCUSSION: The low storage pH of the samples is intended to slow the breakdown of the leached sample components. For extended storage periods, refrigeration of the samples is also recommended. The sample Mn and Fe concentrations may be higher than the standards. In these cases the samples are further diluted. Acetic acid concentration in the standards and samples must match. Hydrogen peroxide is not included in the blank or standards as in the samples because it decomposes during the reaction and forms water.

SPECIAL PROBLEMS AND SUGGESTIONS: After the 24 hour reaction period, some highly organic samples may have dense suspensions of material in them. The sample is filtered or centrifuged to remove the suspension. As all organics are not decomposed by this method, the percentage efficiency of the leach cannot be determined.

REFERENCES: Presley, B.J., Kolodny, Y., Nissenbaum, A., and Kaplan, I.R., 1972. Early diagenesis in a reducing fjord, Saanich inlet, British Columbia - II. Trace element distribution in interstitial water and sediment. *Geochimica et Cosmochimica Acta*, 36: 1073-1090.

## LIGNIN TEST

ABSTRACT: A semi-quantitative analysis for lignin is used as a measure of wood content in sediments. Lignin is detected visually using a lignin-specific stain. Stained samples are compared with stained standards that contain a known amount of wood. The detection limit is 2 ppt wood.

EQUIPMENT: Bifocal, field microscope capable of 120 X magnification  
Slides  
Black grid cardboard slides  
Millipore filter paper

REAGENTS: 1, 3, 5 - trihydroxybenzene  
Concentrated hydrochloric acid (HCl)  
Methanol  
Sawdust

A 10% trihydroxybenzene in methanol solution is made by dissolving 2.5g of trihydroxybenzene in 25 ml methanol. The test solution is made by diluting 2.5 ml of 10% trihydroxybenzene to 25 ml with concentrated HCl.

STANDARDS: Standards are made by mixing weighed amounts of sawdust with weighed amounts of wood-free sediments. Standards containing 2ppt, 5 ppt, 1%, 2%, 5%, 10% and 20% wood in sediment (w/w) were found to be sufficient to cover the range of values found in most samples.

### PROCEDURE:

Equipment Preparation: Clean microscope and adjust the lighting. The microscope is set at 60X magnification.

The slides are prepared by glueing the whitemillipore paper to the black grid cardboard slides for a field reference gradient.

Sample Preparation: The dried, lightly pulverized sediment samples are poured into a clean tray and mixed to homogenize them. Three representative samples

are then placed in approximately 10 mg portions on the grid slides for examination. The standards are similarly prepared. Both samples and standards are tinted by 1 to 2 drop additions of the test solution, and covered with a glass slide and allowed to dry at room temperature.

Analysis: Lignin is stained dark red by the test solution. Using the microscope, stained samples are compared with stained standards with respect to relative amounts of stained and unstained areas. Estimates of wood content are made from the comparison. Three determinations are made for each sample.

Statistical Information: The detection limit is 2ppt. The coefficient of variation in samples that contained no detectable wood was 0% in samples containing wood, this was approximately 50%. This high value is caused in part by the heterogeneous nature of wood particles in sediments.

The method was evaluated using an F-test based on eight replicate analyses of eight samples (Till, 1974). This showed that the difference between different samples was greater than the difference obtained from repeated analysis of one sample at greater than a 99% confidence level.

DISCUSSION: Wood particles usually occur in the sand size or larger fraction of sediments. No lignin could be detected in the fine (less than 63 micrometres) sediment fractions.

The sawdust used in making standards should be similar to what is expected in samples. This allows more accurate estimate of wood content from the lignin content because different kinds of wood contain different amounts of lignin; this is generally around 20%. Approximately 50 samples can be prepared and analyzed in one day.

SPECIAL PROBLEMS AND SUGGESTIONS: The trihydroxybenzene in hydrochloric acid should only be made up as required. Both stages of the test solution should be stored in the dark because they decompose in the presence of light.

Millipore paper was always used as ordinary paper does not work as well. The test reagent does act on the Millipore paper as well, turning it pink. Only strands of dark red are positive indicators of the presence of lignin. The standards can be used for calibrating all the samples done in a work week. Fading hinders their use after that period.

REFERENCES: Pocklington, R. and MacGregor, C.D., 1973. The determination of lignin in marine sediments and particulate form in seawater. *Intern. Journal of Environmental Analytical Chemistry*, 3: 81-93.

Pocklington, R. and Hardstaff, W.R., 1974. A rapid semi-quantitative screening procedure for lignin in marine sediments. *Journal Cons. int. Explor. Mer.* 36 (1): 92-94.

Till, R., 1974. *Statistical methods for the earth scientist.* Halstead Press, John Wiley and Sons Ltd., New York, U.S.A., 154 pp.

## TOTAL AND ORGANIC CARBON

ABSTRACT: A Leco WR-12 analytical system is used to determine total and organic carbon in sediment samples. This system utilizes an induction furnace for combustion. The carbon as carbon dioxide is absorbed on a molecular sieve from which it is removed and measured by a thermal conductivity detector which is in turn calibrated to a standard. The system provides an automated carbon analysis in one minute with a high precision.

EQUIPMENT: Balance - preferably Top-Loading (0.001 g)  
Drying Oven  
Leco Heavy Duty Crucibles  
WR-12 Leco System Including Induction Furnace

REAGENTS: Hydrochloric Acid (6N)  
Distilled Water  
Copper and Iron Chip Accelerator  
Sulphuric Acid  
Magnesium Perchlorate  
Manganese Dioxide  
Set of Leco Iron Ring Standards

STANDARDS: Iron rings 1.000 g of various carbon content are manufactured by Leco. A selection of these rings within the anticipated range of the samples is used to calibrate the system. The iron rings however should be accompanied by a natural sediment standard of known organic and inorganic carbon content.

An iron ring is first burned on the calibrate mode; then another is analyzed on the operate mode. Results should agree to within 5%.

### PROCEDURE:

Equipment Preparation: This is as per manufacturers instructions. It is however best to change the moisture traps between the furnace and detector every day. The cloth dust trap and combustion tube should be cleaned every 25 analyses or as found necessary by dust accumulation.

Sample Preparation: Wet sediment samples are dried at approximately 60°C. When dry, samples are pulverized to a fine powder and aliquots (100 mg or 250 mg) are weighed out into crucibles. Samples are then analyzed for total carbon. For organic carbon analysis, hot (80°C) HCl is added to the samples to remove carbonate. The acid is evaporated off or suctioned through the porous crucibles. Additional hot HCl is added as required until there is no evidence of effervesence from carbonate dissolution. Following the acid wash the samples are washed at least three times with distilled water. The crucibles are then oven dried at approximately 60°C.

Prior to analysis the samples are given a scoop of iron and a scoop of copper accelerator to provide a mass for the combustion in an induction furnace.

Analysis: The crucibles are placed in the induction furnace and the automated system provides a four digit display of the carbon content in the sample as referenced to the selected calibration standards.

Statistical Information: The analytical system has two detection ranges 0.0050-0.2000 and 0.010-5.000 percent, which is precise to approximately 5%.

The digital output must be multiplied by a factor usually 10 or 4 to correct for the sample weight (100, 250 mg, etc.) which is less than the one gram weight of the standard iron ring.

DISCUSSION: This is only one of several automated systems available. Procedures vary slightly for different instruments.

SPECIAL PROBLEMS AND DISCUSSION: Leak checks in the system must be carried out with caution using a commercial leak detector fluid. The sulphuric acid scrubber should be isolated from the system to avoid an acid splash or blow-out during the process of leak checking.

It is necessary to adhere to the manufacturer's electronic checkout procedure and to follow the prescribed maintenance schedules, e.g. trap cleaning and replacement to ensure precise and accurate carbon determinations.



## ORGANIC MATTER EXTRACTIONS AND CHARACTERIZATIONS

ABSTRACT: Sediment hydrocarbon components are fractionated and identified by a combination technique of solvent extraction and gas chromatography. The percentage of solvent extractable materials of the total hydrocarbon composition is also determined. The precision is good in the ppm range and the data analysis is done by a computer program.

EQUIPMENT: Grinder

### **Boiling Flasks**

Length   Diameter

55 cm X 5 cm   Column I's - Soxhlet extraction - distillation with cellulose thimbles

30 cm X 2 cm   Column II's - Separation column chromatographic

40 cm X 1 cm   Column III's - Separation column chromatographic

Drying apparatus

Gas chromatograph with Column OV-101

REAGENTS: Benzene

Pentane

Methanol

Hyflosupercel

Silicagel and Alumina

PROCEDURE A: Organic Matter Extractions and Characterizations

Equipment Preparation: The Column I's are enclosed by an aluminum housing to help contain the treat for the extraction process. The Column II's are cleaned with pentane and filled with fresh hyflosupercel every three or four runs. The Column III's are cleaned with methanol and filled with fresh Silica gel and Alumina each run. The weights of all the collection flasks are prerecorded.

Sample Preparation: Oven dry the samples at 80°C for 8 hours. A power grinder is used to pulverize the samples and 100 g aliquots are weighed out into cellulose extraction thimbles.

Analysis: This procedure is summarized in the following flow chart.

The sediment organic fraction is extracted with a 90:10 mixture of benzene: methanol by boiling the mixture below the thimble's column in a closed Soxhlet apparatus. After 18 hours, the sediment samples are taken out and the distilling is continued until five to ten ml of the extract-containing residue is left in the boiling flask. To the boiling flask is added 50-75 ml of pentane (to precipitate the asphaltene fraction). The samples are transferred from the Column I's to the Hyflosupercel-filled, vacuum-draw Column II's. Approximately 100 ml additions of pentane are made through the column to elute down the soluble fraction. The flow through material is collected in a clean recepticle cup. This is dried (35°C for 8-16 hrs), and weighed to determine bitument content. Alternate additions of benzene and methanol are then run through the Column II's in approximately 100 ml volumes (to re-dissolve the asphaltenes). This is collected in a cup, dried at 35°C for 8 to 16 hrs and then weighed to determine asphaltenes. The pentane soluble material (bitumens) is further fractionated by column chromatography. The silica gel and alumina in a 50:50 mix in the Column III's are used to separate the redissolved pentane fraction. The pentane-dissolved fraction is put through Column III and eluted with 30 ml portions of pentane. The extract is retained in a collection cup, dried and weighed to determine the content of saturates. Thirty ml of benzene is added to the Column III's. This is collected, dried and weighed to determine aromatics. Thirty ml of methanol is added to the Column III's. This is collected, dried and weighed to determine the content of NSO compounds (nitrogen, sulphur and oxygen). The saturates are put through the Gas Chromatograph to determine the n-alkanes.

PROCEDURE B: Gas Chromatography Characterizations

Equipment Preparation: The samples are injected by stringe from the bottle or from a sample concentrator. The concentrator is made from a Pasteur pipet by cutting off the tip leaving a narrow and wide end. The narrow end is flame-sealed so that the sample may be forced to the bottom and contained. The type of column used is an OV-101 capillary tube with a temperature range of 50-250°C. At a chromatograph working temperature of 300°C, life expectancy is not as long. The chromatograph is operated according to the manufacturer's manual. The settings used are: Temperature range 80-300°C; Temperature increment 5°C/minute; Gas flow pressure Z-4 p.s.i.; Attenuation straight line injection 5, concentrator 8-32 and sample volume 0.1-1.0 µl.

Standardization: To identify the peaks of a given sample, the Gas Chromatograph is standardized with an oil containing the necessary range of n-alkanes. Definite identification of pristone and phytone peaks is established, appearing on C<sub>17</sub> and C<sub>18</sub> respectively. The other peaks are identified by their times of integration.

Sample Preparation: In the concentrator method, the sample is dissolved in benzene (three or four drops as required) and it is transferred to the concentrator by a Pasteur Pipet. After washing the sides of the concentrator down with 6.0 µl. C<sub>9</sub> n-alkane, the sample is slowly dried in the tube. If sufficient volume of sample is originally attained, the addition of C<sub>9</sub> is omitted.

Analysis: Part of the samples from one or the other of the preparation techniques is injected into the chromatograph using a 1.0 or 2.0 µl stringe and the results are plotted by the attached chart recorder.

DISCUSSION: The computer program that classified the data (see following diagram), adjusts for the portion of the pentane fraction that is absorbed by the Column III's. The saturates and aromatics make up the hydrocarbons, and the asphaltenes and NSO compounds make up the non-hydrocarbons. The weights of the saturates, aromatics and NSO compounds together should approximate the weight of bitumen.

SPECIAL PROBLEMS AND SUGGESTIONS: The redissolved pentane fraction must be less than 0.050 g when it is added to the Column III's in order for it to pass through the packing. If the sample is over 0.050 g then some of it must first be removed. If the sample weighed into the extraction thimble is less than 100 g, then all calculations and additions are adjusted according to the amount available in the thimble. The drying phase between Columns II and III may take from 8 to 16 hours depending on whether or not water from the air has combined with the methanol in the solution.

Gas Chromatography: Any contamination of the septum at high temperature is overcome by preheating the septum for two days at 200-250°C while operating the gas chromatograph. The injection port is cleaned every two weeks to remove any deposit build-up. The manufacturer's manual is consulted for this. The manufacturer's manual also describes the cleaning operation which is required for the detector every two to three months.

Occasionally some silica gel will pass through into the fractions collected from Column III yielding a sum of the fractions greater than the whole.

CADMIUM ANALYSIS FOR SEDIMENTS

ABSTRACT: A strong acid leach is used to remove Cd from sediments. With this procedure good precision can be attained for concentrations below 2 ppm.

EQUIPMENT: Drying oven  
Balance (0.001 g)  
Teflon bombs (20 ml)  
Heating element  
Atomic absorption spectrophotometer and chart recorder

REAGENTS: Nitric acid (16 N)  
Deionized distilled water (18 mega ohms per cm resistivity)

STANDARDS: A standards additions method is used. This has the advantage that sample and standard matrices are identical, so any interferences are present in both. This method is described in any analytical reference book, for example, see Slavin, 1968.

Stock Cd solution (1000 ppm) is made by dissolving Cd metal in a small amount of concentrated HCl and diluting to volume with deionized distilled water.

PROCEDURE:

Equipment Preparation: The spectrophotometer is set up and operated according to the manufacturer's manual.

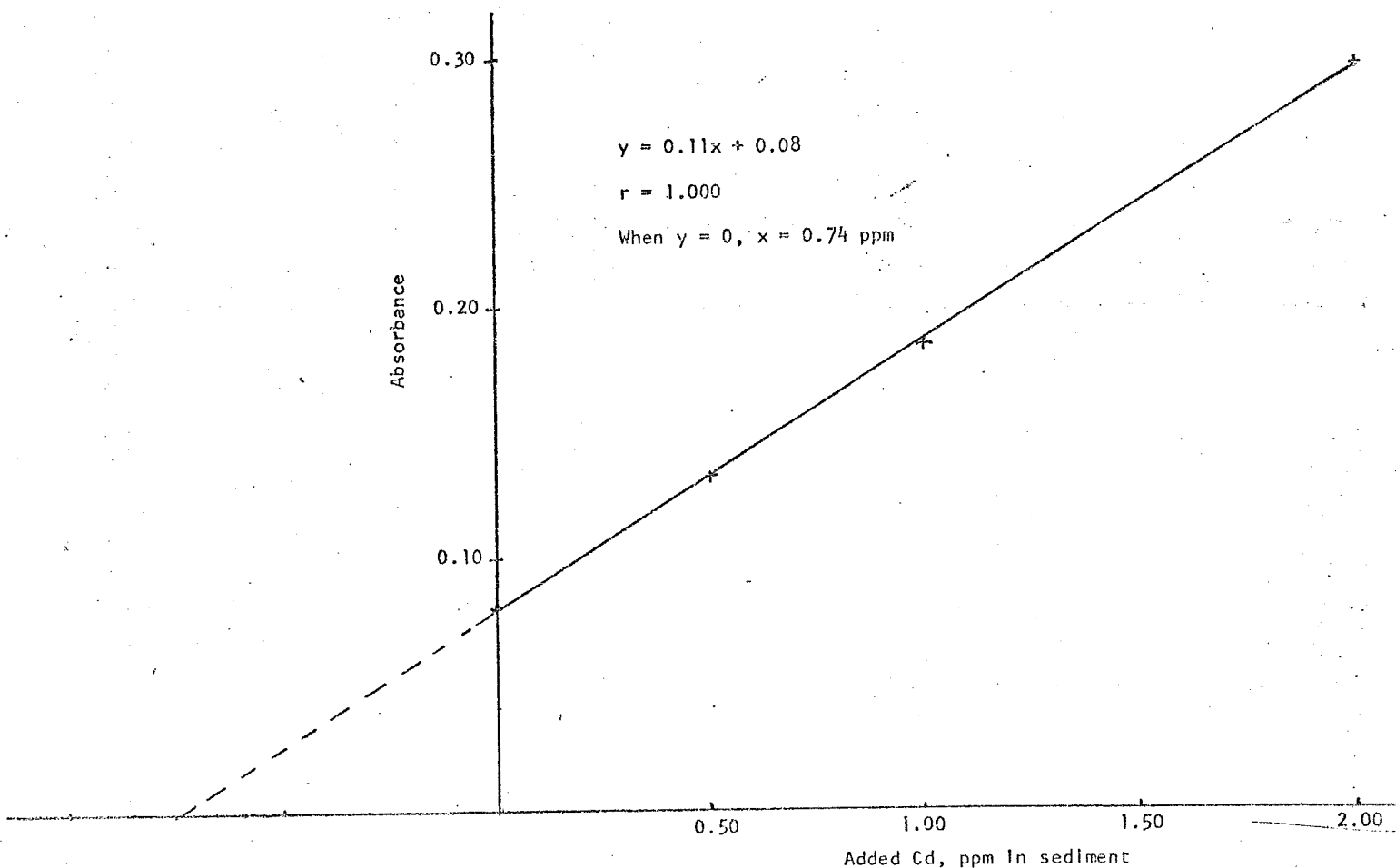
Sample Preparation: The wet sediment samples are dried at 50°C for 24 hours. They are lightly pulverized and weighed out in 2.500 g portions. For each sample, four teflon bombs are used and to each is added 10 ml of 16 N nitric acid. The weighed out portions of 2.500 g are deposited into the bombs. To three of the teflon bombs are added standard additions of a stock Cd solution to give Cd concentrations equivalent to 0.50, 1.00 and 2.00 ppm in the sediment. The four bombs are sealed and heated at 90°C for 24 hours. They are cooled to 20°C and supernatant is diluted with deionized distilled water to 25 ml. to give a rock dilution of ten times. The storage concentration of the analyte is 6.3 N

nitric acid and therefore should be stable.

PROCEDURE

Analysis: The samples are aspirated into the spectrophotometer and their results are plotted on the chart recorder. Between samples, the baseline aspirate deionized distilled water is injected. 6.3 N nitric acid is used as a blank. Because the resonance line for Cd is in the far UV region, signals due to background scattering can be obtained. This must be taken into account and one method for doing so is described below.

Statistical Information: The absorbance results of the spectrophotometer are plotted in a least squares' regression against the added concentration of Cd in the samples. The Cd concentration determined for zero addition of Cd using the regression equation is the concentration in the sediment. A diagram to illustrate this procedure follows.



DISCUSSION: The low drying temperature of the samples and the solid addition to the bombs following the acid addition help prevent volatilization and the resultant loss of the Cd in the samples.

The reported leaching efficiency in reported Cd sediment literature is set at 60-85% (Jones, 1973; Holmes, et al., 1974). However, those systems used open reaction techniques while this method is dependent on a closed technique, hence, higher percentage leaching is expected.

The total digestion method used for other trace metals was not applicable to Cd analysis because of the very low concentrations of Cd present relative to the other trace metals. Cd could not be detected with this technique because of high background signals (nonspecific absorption and scattering) caused by the sediment matrix.

SPECIAL PROBLEMS AND SUGGESTIONS: Non-specific background absorption is accounted for by using the non-specific 220 nm line with the Pb lamp. Any recording obtained from the spectrophotometer at this line must be caused by non-specific absorption and is subtracted from the Cd line. This procedure is described by Kahn et al., 1972. Every sample must be checked this way as the background can vary from one to the other. This check is superior to using the Background Corrector with the spectrophotometer because no loss of sensitivity results.

Frothing during the leaching phase is found to be greatest when examining samples that contain large amounts of calcium carbonate.

REFERENCES: Holmes, C.W., Slade, E.A. and McLerran, C.J., 1974. Migration and redistribution of zinc and cadmium in marine estuarine system. *Environmental Science and Technology*, 8: 255-259.

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Kahn, H.C., Fernandez, F.J. and Slavin, S., 1972. The determination of lead and cadmium in soil and leaves by atomic absorption spectrophotometry. Atomic Absorption Newsletter, 11: 42-45.

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## CADMIUM ANALYSIS FOR SEDIMENTS

ABSTRACT: A strong acid leach is used to remove Cd from sediments. With this procedure good precision can be attained for concentrations below 2 ppm.

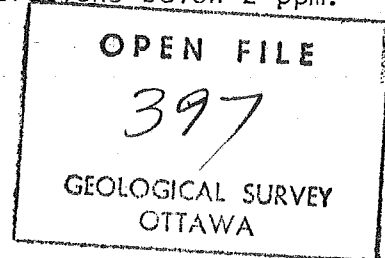
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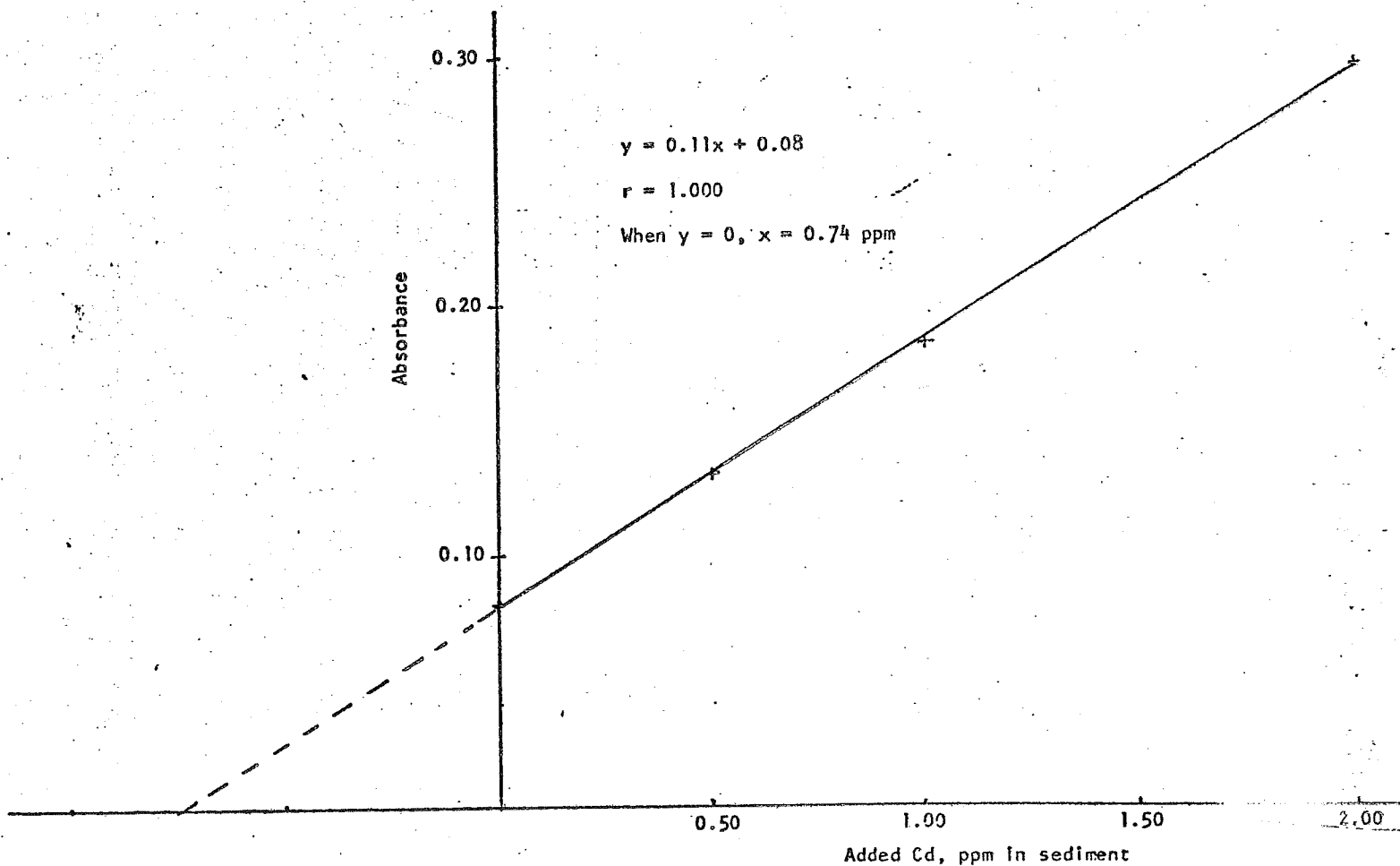
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