

TECHNIQUES IN MARINE ENVIRONMENTAL SCIENCES

No. 9

Sediments and suspended particulate matter: Total and  
partial methods of digestion

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INTERNATIONAL COUNCIL FOR THE EXPLORATION OF THE SEA  
CONSEIL INTERNATIONAL POUR L'EXPLORATION DE LA MER

Palægade 2-4, DK-1261 Copenhagen K, Denmark

November 1990

ISSN 0903-2606



## SEDIMENTS AND SUSPENDED PARTICULATE MATTER: TOTAL AND PARTIAL METHODS OF DIGESTION

### 1 INTRODUCTION

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

This leaflet describes in detail the wet chemical methods for both total decomposition and weak acid extraction of sediments and suspended particulate matter.

#### 1.1 Total decomposition methods

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

Hydrofluoric acid decomposition has the following advantages:

- (a) HF is the only acid that completely dissolves the silicate lattices and releases all the associated metals, such as Al, Fe, and Li, used for the grain size normalization of the data;
- (b) Accuracy can be assessed by analyzing reference materials certified for the total metal content; and
- (c) Intercomparable data, free from operationally defined bias, can be obtained.

Some laboratories have been reluctant to use HF due to its corrosive nature. In our experience, after using HF for 28 years, HF poses no greater danger than other strong acids when normal laboratory safety rules for handling acids are observed.

#### 1.2 Non-HF digestions

##### 1.2.1 Strong acid digestions

Strong acid digestions using nitric acid ( $\text{HNO}_3$ ) or aqua regia ( $\text{HNO}_3 + \text{HCl}$ ) are commonly used to decompose marine sediments. They are NOT recommended for the following reasons:

- (a) Strong acid digestions without HF result in incomplete digestions because silicates and other refractory oxides are not completely dissolved;
- (b) The proportion of metals dissolved is variable and depends on the sample type, matrix, and element;

- (c) Accuracy of the results cannot be determined since no reference materials are certified for strong acid digestions; and
- (d) Metal data obtained from strong acid digestions are not intercomparable with total metal data and are subject to operationally defined bias.

### 1.2.2 Moderate and weak acid extractions

Moderate or weak acid extractions, such as hydrochloric acid (HCl) and acetic acid (HOAc), are often used for chemical partition studies (Loring, 1978, 1981). They are strictly operationally defined. The acetic acid (HOAc 25% v/v) extraction procedure is described in Section 3 (marine sediments) and Section 5 (suspended particulate matter), below.

The main disadvantages of moderate and weak acid single or sequential extractions are:

- (a) The proportion of metals dissolved is variable and depends on the sample type, matrix, and element;
- (b) Accuracy of the results cannot be determined since no reference materials are certified for moderate and weak acid digestions; and
- (c) Metal data obtained from moderate and weak acid digestions are not intercomparable with total metal data and are subject to operationally defined bias.

## 2 TOTAL (HF) DECOMPOSITION OF SEDIMENTS

In this method, hydrofluoric acid and aqua regia are used to release the total metal content from marine sediments into solution in a sealed Teflon decomposition vessel, referred to as a Teflon bomb. The Teflon bomb decomposition procedure is shown in detail in the videotape that can be obtained from ICES to accompany this leaflet. It has also been described by Rantala and Loring (1973, 1975, 1987) and it is the method recommended for the ICES intercalibration exercise (Loring, 1987).

The main advantages of the Teflon bomb decomposition are:

- (a) Rapid decomposition;
- (b) Reduced risk of contamination;
- (c) Small volume of acid required; and
- (d) No loss of volatile elements.

### 2.1 Apparatus and reagents

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

### 2.1.1 Teflon bomb construction

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

### 2.1.2 Teflon bomb heating equipment

The Teflon bomb in which the sediment sample is decomposed is heated either in boiling water or, in a more recent development, in a microwave oven (Rantala and Loring, 1989) to provide the necessary heat and pressure for the total decomposition of the sample.

(a) For heating the bomb by submersion in boiling water:

Hotplate

Covered ceramic dishes (25 cm x 25 cm x 10 cm deep). Each dish can accommodate 8 bombs at a time.

(b) For microwave heating:

Microwave pressure cooker. Each cooker will accommodate 4 bombs at a time.

Flat-based microwave-safe dish to compensate for the concave bottom of the cooker

Beaker, 100 ml

Microwave oven with turntable

The microwave oven should be calibrated to detect any decrease in the power output in the future and to facilitate the calculation of the optimum heating time for samples. The calibration is carried out by measuring the temperature rise of 1 liter of distilled water in a beaker with the oven set at full power for 2 minutes. The temperature rise from room temperature was found to be 20.9 °C for the microwave oven (Panasonic Model NE-7970C with 700W full capacity) used in our laboratory.

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

The heating time depends on the power output of the microwave oven and the load. The optimum heating time can be estimated (Kingston and Jassie, 1986) and verified experimentally by analyzing certified reference materials and comparing the results with those obtained by a 1-hour decomposition in boiling water.

Teflon bombs without pressure relief should not be used for microwave heating owing to the potential danger of over-pressurization.

### 2.1.3 Laboratory equipment

Mechanical shaker  
Analytical balance  
Agate mortar and pestle

### 2.1.4 Labware

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

No glassware should be used in the presence of HF, even when the corrosive nature of HF is diminished when complexed with boric acid ( $H_3BO_3$ ), because contamination might be released from the glassware.

All labware should be thoroughly cleaned by first soaking for 24 hours in dilute nitric acid and then rinsing with de-ionized water.

### 2.1.5 Reagents

Hydrofluoric acid [HF]	(49%)
Nitric acid [ $HNO_3$ ]	(70%)
Hydrochloric acid <sup>3</sup> [HCl]	(37%)
Aqua regia [ $HNO_3 + HCl$ ]	(1:3 v/v)
Boric acid crystals [ $H_3BO_3$ ]	
De-ionized distilled water	

All reagents must meet ACS analytical reagent grade requirements.

### 2.1.6 Sample size

The size of sample required is dependent mainly on the expected metal concentrations. In general, a 0.1 gram sample is used for the major elements and a 1 gram sample is used for trace metal determinations if only flame AAS is available. A 200 mg sample containing normal amounts of major and trace metals, however, has been found to be sufficient for most metal concentrations if the sample is homogeneous and graphite furnace AAS is available. Certain trace metals occurring in very low concentrations may require larger sample sizes.

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

## 2.2 Total decomposition procedure

- (a) Accurately weigh 100-1000 mg (100-200 mg for microwave heating) of finely ground sample;
- (b) Transfer to a Teflon bomb;
- (c) Add 1 ml of aqua regia ( $\text{HNO}_3$  :  $\text{HCl}$ , 1:3 v/v);
- (d) Add 6 ml of HF very slowly to avoid excessive frothing;
- (e) Close the bomb tightly and submerge in boiling water for a minimum of 1 hour;  
  
OR place the bomb in the microwave pressure cooker; place the cooker along with a beaker containing 50 ml of water in the microwave oven; heat for 60 seconds at full power (700 W);
- (f) Remove the bomb from the heat source and cool it to room temperature in cold water or an ice bath;
- (g) Weigh 5.6 g of  $\text{H}_3\text{BO}_3$  and transfer into a 100 ml polypropylene volumetric flask;
- (h) Add 20 ml of  $\text{H}_2\text{O}$  and shake briefly;
- (i) Remove the bomb from the cooling water, and dry it;
- (j) Open the bomb (be sure to wipe off any water found on the outside of the sealing area) and transfer the contents into the 100 ml polypropylene flask;
- (k) Rinse the bomb several times with de-ionized water and add the rinsings to the flask;
- (l) Shake the flask to complete the dissolution (black carbon residue may remain but does not contain significant amounts of metals and does not interfere with subsequent metal determinations);
- (m) Make the solution up to 100 ml with  $\text{H}_2\text{O}$ ;
- (n) Transfer the solution into a polypropylene bottle for storage;
- (o) Allow solutions obtained from 100-500 mg sample sizes to settle overnight; those from 500-1000 mg sample sizes should settle for several days in case borosilicate forms. This is because the metals cannot be determined in concentrated solutions (>500 mg sample/100 ml) until the gelatinous precipitate of borosilicates has settled, leaving a clear surface layer that can be analyzed. This process may take 7-14 days. When a smaller sample is used (<500 mg sample/100 ml), such precipitation will not occur and the sample may be analyzed after the black carbon residue has settled overnight;
- (p) Analyze the solutions for trace metals by flame or graphite furnace AAS.

### 2.2.1 Storage of sample solutions

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

## 3 ACETIC ACID (HOAc) EXTRACTION OF SEDIMENTS

Selective chemical methods have been developed to partition the total metal concentrations into their loosely bound (non-detrital) and residual (detrital) phases. Such fractionation allows us to make some deductions as to the carriers, transport mode, and potential bio-availability of metals entering and within these different systems (Loring, 1981).

The acetic acid method was chosen because it is one of the weakest chemical treatments that can be used to remove effectively the weakly bound part of the total metal concentrations in sediments (Loring, 1978) and particulate matter (Loring *et al.*, 1983, 1985). It removes metals held in ion exchange positions, easily soluble amorphous compounds of iron and manganese, carbonates, and those weakly held in organic matter. The concentration of the metal determined in this fraction is operationally defined as the non-detrital (acid soluble) fraction because it leaves the silicate lattices intact and does not attack the resistant iron and manganese minerals or organic compounds. The proportion of a metal remaining in this residual fraction is referred to as the detrital (acid insoluble) fraction of the material.

### 3.1 Apparatus and reagents

#### 3.1.1 Laboratory equipment

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

#### 3.1.2 Labware

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

#### 3.1.3 Reagents

- Glacial acetic acid [HOAc], 25% v/v (ACS analytical grade)

### 3.2 Extraction procedure

(a) Place a portion of dry sample in an agate mortar. Do not grind it. Simply crush the lumps;

- (b) Weigh 2 grams of sample and transfer it into a polypropylene centrifuge tube;
- (c) Weigh the tube + the sample and record the weight;
- (d) Add 25 ml of 25% v/v HOAc;
- (e) Cap the tube and shake slowly in a mechanical shaker for 6 hours;
- (f) Balance the centrifuge tubes and centrifuge for 10 minutes at 2500 RPM or until the supernatant is clear;
- (g) Pour the supernatant HOAc into a 50 ml volumetric flask;
- (h) Wash the sediment with 10 ml of water and shake the tube briefly on the shaker;
- (i) Separate the wash water by centrifuging and add it to the flask;
- (j) Rinse the funnel and make up the HOAc solution to a volume of 50 ml;
- (k) Dry the tube containing the residue in the oven at 110 °C and place in the desiccator to cool;
- (l) When the tube reaches room temperature, weigh it and calculate the percent by weight contribution of the residual fraction;
- (m) Transfer the dry residue to the mortar and use a portion of the ground-up sample for the HF Teflon bomb decomposition to determine the trace metals held in the acid insoluble or detrital fraction of the sediments;
- (n) By flame or graphite furnace AAS, analyze the acetic acid soluble and residual solutions for trace metals.

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

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

For example: Zinc

Let:

Sample weight for HOAc leach	=	2.00 g
Weight of HOAc residue	=	1.80 g
Weight of residue for decomposition	=	0.30 g
Volume of flask for HOAc solution	=	50 ml
Volume of flask for decomposition solution	=	100 ml
Concentration of Zn in HOAc solution	=	0.20 µg/ml
Concentration of Zn in decomposition solution	=	0.25 µg/ml

$$\text{Non-detrital contrib. of Zn} = 50/2.000 \cdot 0.20 = 5 \mu\text{g/g}$$

$$\text{Detrital contrib. of Zn} = 1.800/2.000 \cdot 100/0.3 \cdot 0.25 = 75 \mu\text{g/g}$$

Therefore:

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

#### 4 TOTAL HF DECOMPOSITION OF SUSPENDED PARTICULATE MATTER

Suspended particulate matter (SPM) samples for metal analysis are carefully collected by filtration on pre-cleaned and pre-weighed Nuclepore filters, washed free of salts, dried, and reweighed. (For details of the collection and preparation of SPM for gravimetric and trace metal analysis, see Yeats and Brüggmann, 1990.)

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

##### 4.1 Apparatus and reagents

For the suspended particulate matter decomposition, the same Teflon bombs and heating equipment are used as described in Sections 2.1.1 and 2.1.2, above.

##### 4.1.1 Laboratory equipment

Mechanical shaker  
Microbalance (readability 0.01 mg)

##### 4.1.2 Labware

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

##### 4.1.3 Reagents

Hydrofluoric acid [HF]	(46%)
Nitric acid [HNO <sub>3</sub> ]	(71%)
Hydrochloric acid <sup>3</sup> [HCl]	(37%)
Aqua regia [HNO <sub>3</sub> + HCl]	(1:3 v/v)
Boric acid crystals [H <sub>3</sub> BO <sub>3</sub> ]	
De-ionized distilled water <sup>3</sup>	

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

##### 4.1.4 Sample size

The amount of SPM sample required for precise and accurate determinations of the elements will depend on their concentrations in the SPM. A minimum of 1 mg (dry weight) is usually required to determine most of the metals at their natural background levels.

#### 4.2 Total decomposition procedure

- (a) Transfer a filter into a Teflon bomb with plastic tweezers and squash it into the bottom of the vessel;
- (b) Add 1 ml of aqua regia, 1 ml of HF, and close the bomb tightly;
- (c) Submerge the bomb in boiling water for 1 hour, or heat for 40 seconds in a microwave oven (for further details, see Section 2.2, above);
- (d) After cooling, decant the contents through a polypropylene funnel into a 25 ml polypropylene volumetric flask containing 0.93 g of boric acid and approximately 5 ml of water. If necessary, a more concentrated solution can be obtained by using 0.5 g of boric acid and making the solution up to 10 ml in a polypropylene storage bottle by weighing;
- (e) Wash the filter remaining in the Teflon bomb several times with small volumes of water, each time collecting the washings in the 25 ml flask (some broken pieces of the filter may enter the flask, but will settle and do not interfere with subsequent metal determinations);
- (f) Finally, shake the volumetric flask to complete the dissolution and make up to 25 ml with de-ionized water;
- (g) Prepare the blank solution in the same manner, omitting the sample;
- (h) Store the solutions in polypropylene bottles;
- (i) Analyze the solutions for trace metals by flame or graphite furnace AAS.

#### 5 ACETIC ACID EXTRACTION OF SPM

The chemical technique to partition the particulate metals into their non-detrital and detrital phases involves the leaching of the particulate matter on Nuclepore filters with 25% v/v acetic acid in a modified Millipore Sterifil vacuum filtration apparatus (see Figure 1). The residue remaining on the filters is decomposed with a combination of ultra-high purity hydrofluoric acid and aqua regia in the Teflon bombs (Rantala and Loring, 1985).

##### 5.1 Apparatus and reagents

###### 5.1.1 Extraction apparatus

Polycarbonate Millipore Sterifil vacuum filtration funnel and receiver flask attached to a polypropylene Millipore 'Swinnex'-

47mm filter holder base (Figure 1) \*

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

Vacuum pump

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

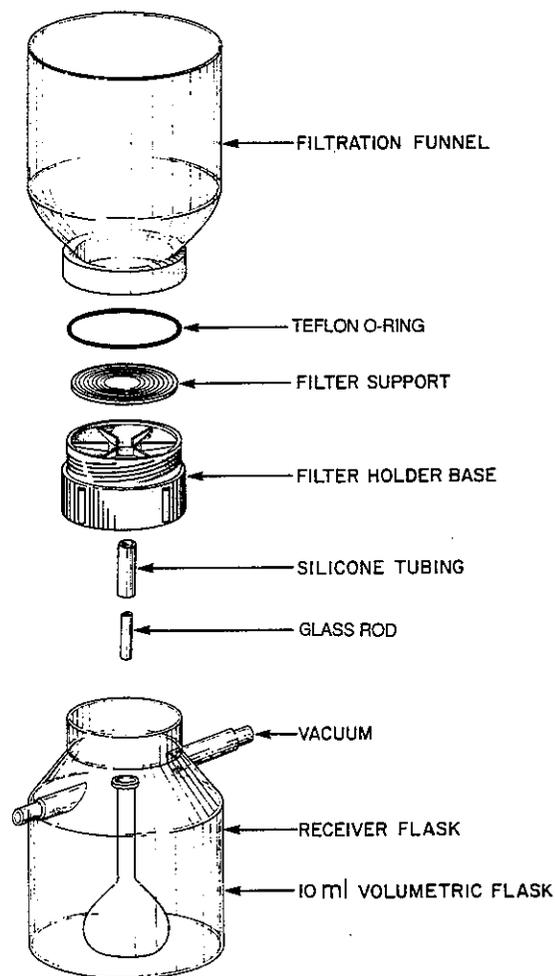


Figure 1. Apparatus for acetic acid extraction (modified from Rantala and Loring, 1985).

### 5.1.2 Labware

Glass volumetric flasks, 10 ml  
 Polypropylene narrow mouth bottles  
 Polypropylene funnel  
 Plastic tweezers

### 5.1.3 Reagents

Glacial acetic acid [HOAc] 25% v/v ultra-high purity  
De-ionized distilled water

### 5.1.4 Sample size

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

## 5.2 Extraction procedure

- (a) Center the sample filter and lay it flat on the moistened filter support;
- (b) Screw the filtration funnel on tightly to the base and insert the glass rod into the silicone tubing;
- (c) Attach the filter holder base to the receiver flask;
- (d) Place 5 ml of 25% v/v acetic acid in the funnel;
- (e) Cover the funnel and let stand for 24 hours;
- (f) After 24 hours, remove the glass rod and quickly insert the silicone tubing into a 10 ml volumetric flask placed in the receiver flask (no loss of acetic acid solution from the tubing before its insertion into the flask will occur unless the filter has been pierced or badly seated on the support);
- (g) Apply vacuum to the receiver flask;
- (h) After all the acetic acid has been filtered, wash the filter twice with 2 ml of water, each time applying vacuum;
- (i) After the final wash, remove the funnel and transfer the filter to a Petri dish for drying at 60 °C;
- (j) Under vacuum, suck the rest of the filtrate trapped in the filter holder into the flask;
- (k) Make the flask up to a volume of 10 ml with water, transfer the solution into a polypropylene bottle, and store for AAS analyses;
- (l) Treat the Nuclepore filter blanks in the same manner;
- (m) Decompose the residual matter on the dried filters with HF + aqua regia (see Section 4.2, above).

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