TECHNIQUES IN MARINE ENVIRONMENTAL SCIENCES

No. 3

Cadmium in marine sediments: Determination by graphite furnace atomic absorption spectroscopy

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CONSEIL INTERNATIONAL POUR L'EXPLORATION DE LA MER

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

December 1987

ISSN ●●●●-●●●● 2707-6997
ISBN 978-87-7482-258-5
https://doi.org/10.17895/ices.pub.5029

CADMIUM IN MARINE SEDIMENTS: DETERMINATION BY GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROSCOPY

1 INTRODUCTION

Cadmium is one of the most important toxic elements to be determined in environmental samples. Cd has proved, however, to be a difficult element to determine with good precision and relative accuracy. This is shown by the results of recent intercalibration exercises.

(a) In the Baltic Sediment Intercalibration Exercise, Brügmann and Niemistö (1987) found deviations in reported Cd results unacceptable. Relative standard deviations (rsd's) were 48 % and 63 % for for the two intercalibration samples.

(b) In the National Research Council of Canada (NRCC) intercalibration (NRC MS1/TM), Berman and Boyko (1985) found that less than one-third of the 35 laboratories submitting Cd values appeared competent in handling samples at the 0.6 mg/kg level.

(c) In the ICES First Intercalibration Exercise on the Trace Metals in Marine Sediments (1/TM/MS) report, Loring (1987) found that participating laboratories had difficulty with Cd determinations. Rsd's were 42 %, 39 %, and 53 % for the three intercalibration samples.

It is suggested that the poor results are mostly due to the instrumental methods (Jensen, 1987) and inadequate use of reference materials to ensure good relative accuracy of the results.

This paper discusses the various parameters that affect the precision and relative accuracy of Cd determinations and describes a simple, straightforward method based on the teflon bomb decomposition of the sample with HF-aqua regia followed by a graphite furnace atomic absorption determination of Cd using an uncoated L'vov platform. The relative accuracy and precision of the method has been confirmed and found to be good by analyses of reference materials and through participation in intercalibration exercises.

2 DECOMPOSITION AND ANALYTICAL PROCEDURES

In this method, hydrofluoric acid and aqua regia are used to release the total Cd content from marine sediments into solution in a teflon decomposition vessel referred to as a teflon bomb. The teflon bomb decomposition has been described by Rantala and Loring (1973, 1975) and is the method recommended for the ICES 1/TM/MS intercalibration exercise.

2.1 Apparatus and reagents

2.1.1 Teflon bomb construction

The construction of the bombs to be used must be such that no metallic contamination will occur. LORRAN all-teflon decomposition vessels (Rantala and Loring, 1973) were used by the authors. A decomposition temperature of approximately 100^{0}C has proved to be sufficient.

2.1.2 Labware

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

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

All labware, including the volumetric flasks, should be made of polypropylene or other plastic material.

Although the corrosive nature of HF is diminished when complexed with H_3BO_3, the above precautions should nevertheless be observed.

2.1.3 Reagents

Reagent grade hydrofluoric acid (49 %), hydrochloric acid (37 %), nitric acid (70 %), and boric acid crystals are used in the decompositions. Any distilled water used should be de-ionized.

2.1.4 Standard solutions

Standard solutions are diluted from a 1000 µg/ml stock solution to the appropriate range. Working standards must be in HF decomposition matrices corresponding to the sample solutions. A minimum of three standards should be prepared to allow construction of a calibration curve.

2.1.5 Sample size

The amount of sample used in the decompositions is dependent on the estimated Cd concentration in the sample and how soon the solution must be analysed. For Cd concentrations < 0.2 mg/kg, a sample size of 1 g has been found suitable. However, Cd cannot be determined in concentrated solutions (> 500 mg sample/100 ml) until a gelatinous precipitate of borosilicates has settled leaving a clear surface layer that can be analysed. This process may take several days. When a smaller sample is used (< 500 mg sample/100 ml), such precipitation will not occur and the sample may be analysed after the black carbon residue has settled overnight.

2.1.6 Storage of sample solutions

Sample solutions stored in precleaned polypropylene bottles are extremely stable and it has been possible to determine Cd accurately in a clear surface layer after several years of storage.

2.2 Decomposition

(a) Accurately weigh 100-1000 mg of finely ground sample;

(b) transfer to a teflon bomb;

(c) add 1 ml of aqua regia (HNO_3:HCl, 1:3 v/v);

(d) add 6 ml of HF very slowly, to avoid excessive frothing;

(e) close the bomb and heat at > 90^0C for a minimum of 1 h;

(f) remove from heat and cool to room temperature;

(g) weigh 5.6 g of H_3BO_3 and transfer into a 100 ml polypropylene volumetric flask;

(h) add 20 ml of H_2O and shake briefly;

(i) open the bomb and transfer the contents into the flask;

(j) shake the flask to complete the dissolution (carbon residue may remain);

(k) make the solution up to 100 ml with H_2O;

(l) transfer the solution into a polypropylene bottle for storage;

(m) allow solutions obtained from 100-500 mg sample size to settle overnight; those from 500-1000 mg sample size should settle for several days to observe if borosilicate will form. If it does, use the clear surface layer for the analysis.

2.3 Atomic absorption analysis

The GFAAS determination of Cd requires background correction, use of an uncoated L'vov platform, optimizing instrumental parameters, correct application of appropriate reference materials and, preferably, automatic sample introduction.

2.3.1 L'vov platform

A L'vov platform placed in a graphite tube permits the atomization of the sample under nearly isothermal conditions. This results in the reduction in interferences and permits direct comparison with aqueous standards (Sturgeon et al., 1982). L'vov platforms should be made of uncoated graphite. In earlier work without the platform, Rantala and Loring (1980) found that pyrolytically coated tubes were unsatisfactory for Cd as they produced constantly changing sensitivity and performed well only after > 100 firings. Findings with plat-

forms made in the laboratory from the grooved end of the tube (Hinderberger et al., 1981) confirm that uncoated platforms perform the best. They can be inserted either into coated or uncoated tubes.

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

2.3.2 Automatic sample introduction

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

2.3.3 Sample cups

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

2.3.4 Optimizing the furnace program

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

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

When maximum peak heights are obtained for the standard and the reference material solutions, and if the peak height of the reference material solution is within ±10 % of the standard at the 0.002 µg Cd/ml level (at linear range), the furnace program is considered to be optimized. To assist in optimizing, the following guidelines should be followed:

(a) Drying: the platform requires a relatively high drying temperature approximately 270 ^{0}C. Ramptime must be sufficiently slow to avoid spattering of the sample.

(b) Charring: charring temperature, ramp-, and holdtimes must be optimized to avoid loss of Cd during this cycle.

(c) Atomization: the fastest possible ramptime to atomization temperature should be used. The atomization temperature is determined experimentally.

For example, instruments having a maximum power mode feature such as the Perkin Elmer HGA-500 require temperature control calibration. During calibration, be sure to press the manual temperature button long enough, while adjusting the calibration control. With the platform, the time required to adjust the calibration control at 1600^{0}C could be as long as 30 to 40 seconds.

The furnace program for HGA-500 graphite furnace is shown in Table 1.

3 RESULTS AND DISCUSSION

The detection limit (i.e., the concentration of Cd giving an absorption signal twice that of the blank) was found to be 0.1 µg/l Cd. The precision and accuracy of the method have been verified through analyses of reference materials submitted for intercalibration programmes of various agencies and through participation in intercalibration exercises.

Results obtained by this procedure are compared in Table 2 with accepted ("reliable", "best", "usable", etc.) values for reference materials and with the mean values obtained after rejection of outliers in three intercalibration exercises.

4 CONCLUSION

The method described for the determination of total Cd is uncomplicated and laboratory assistants, inexperienced with this method, have been able to reproduce the Cd concentration ±10 % at 0.2 mg Cd/kg dry sediment in reference materials. The method has also been applied to marine suspended particulate matter (Rantala and Loring, 1985) with good success.

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Table 1. Furnace program.

	Program step				
	1	2	3	4	5
T^0C	270	400	1 600	2 700	20
Ramptime, s	10	20	0	1	1
Holdtime, s	20	20	3	3	15
Internal gas (argon)ml/min	-	-	50	-	-

Table 2. Comparison of Cd values (mg/kg) obtained using this method with values reported for reference materials and samples in intercalibration exercises (s.d. = standard deviation).

Agency	Reference material		Accepted value Cd mg/kg	Value using this method Cd mg/kg
NRCC	BCSS-1	Marine sediment	0.25[a]	0.25[b]
NRCC	MESS-1	Marine sediment	0.59[a]	0.59[b]
USGS	MAG-1	Marine sediment	0.2[c]	0.19[d1]
USGS	DNC-1	Dolerite	0.09[e]	0.086[e1]
USGS	W-2	Diabase	0.10[e]	0.074[e1]
ANRT	GS-N	Granite	0.03[f]	0.037[g]
ANRT	FK-N	Feldspar	0.02[f]	0.019[g]

Intercalibration	Sample		Mean value mg/kg	s.d.	Value using this method mg/kg	s.d.
Baltic Sediment...	ABSS	Marine sediment	0.94	0.45[h]	0.78	0.02[i]
Baltic Sediment...	MBSS	Marine sediment	0.74	0.47[h]	0.58	0.02[i]
NRC MS1/TM	A	Marine sediment	0.71	0.25[j]	0.69	0.01[k]
NRC MS1/TM	B	Marine sediment	0.98	0.22[j]	1.05	0.03[k]
NRC MS1/TM	C	Marine sediment	2.00	0.42[j]	2.08	0.29[k]
ICES/1/TM/MS	A	Marine sediment	1.78	0.74[l]	1.66	0.04[m]
ICES/1/TM/MS	B	Marine sediment	2.05	0.81[l]	1.95	0.10[m]
ICES/1/TM/MS	C	Marine sediment	0.73	0.39[l]	0.52	0.01[m]

[1] Without platform.

[a] Berman, 1981;
[b] Submitted to NRCC;
[c] Abbey, 1983;
[d] Rantala and Loring, 1980;
[e] Flanagan, 1984;
[f] Govindaraju, 1984;
[g] Govindaraju, 1985;
[h] Brügmann and Niemistö, 1987;
[i] Lab 30;
[j] Berman and Boyko, 1985;
[k] Lab 9;
[l] Loring, 1987;
[m] Lab 0.