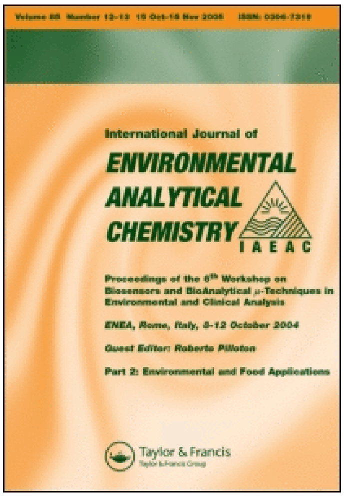

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Partition and Determination of Cadmium, Copper, Lead and Zinc in Marine Suspended Particulate Matter

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Partition and Determination of Cadmium, Copper, Lead and Zinc in Marine Suspended Particulate Matter

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A method for the determination of Cd, Cu, Pb, and Zn in the total and acetic acid (25%) soluble fraction of suspended particulate matter collected on Nuclepore membranes is described. The acetic acid leaching was carried out in a modified Millipore vacuum filtration apparatus. The total sample and the acetic insoluble fraction were decomposed in teflon bombs with HF/aqua regia. Flame or graphite furnace AAS was used for metal determinations. Sequential acetic acid extractions (3) show that on the average 76.4–92.0% of the metals are removed with the first extraction. Cadmium is potentially most easily available to biota with 90.4% of the total metal concentration located in the acetic acid soluble fraction.

KEY WORDS: SPM, heavy metals, HOAc extraction, GFAAS.

INTRODUCTION

Very little is known about the potential and real availability of metallic constituents to marine biota from suspended particulate matter. This is because only a part of the total particulate metal concentrations are held in a "reactive" form that can be easily assimilated by the biota. This paper describes an acetic acid (25%) extraction technique to remove that part of the total particulate metal concentration which might be available to the biota and responsive to physical chemical conditions in the environment.[1]

The acetic acid extraction is significant because it is one of the weakest chemical attacks that can be effectively used to remove metals from sites and forms that are potentially available to biota such as those held in carbonates, ion exchange, and adsorbed positions, amorphous compounds of iron and manganese and those weakly attached to organic matter.[2]

EXPERIMENTAL

Sample collection

The samples used in developing the technique were collected from Tamar Estuary U.K. Aug. 1980.[1]

Surface SPM samples were collected with a polyethylene bucket. The samples were filtered onto preweighed 47 mm, 0.40 μm Nuclepore® membranes and washed with deionized water to remove occluded dissolved sea salt. The filters were dried at 60°C, weighed and stored in plastic Petri dishes.

Apparatus

The extraction apparatus consists of a polycarbonate Millipore Sterifil vacuum filtration funnel and receiver flask attached to a polypropylene Millipore Swinnex—47 mm filter holder base (Fig. 1). It was necessary to replace the red silicone o-ring with Viton A as the silicone o-ring highly contaminated the filtrate with Zn. In addition, some filter supports contained visible metallic particles that released particularly Zn during the leaching. These supports were replaced with new ones that under the microscopic examination were found to be particle free. Silicone tubing was then attached to the filter unit outlet and another piece of tygon tubing was placed over it as a sleeve to avoid contamination from a metal pinchcock used during the leaching. All the components of the filtration unit were leached with 25% acetic acid and several blanks were analysed before the actual sample extraction took place.

"LORRAN" all Teflon pressure decomposition vessels (H. K. Morrison and Sons Ltd. Mount Uniacke N.S., Canada) designed in our laboratory[3] were used to decompose the residual and total material on filters.

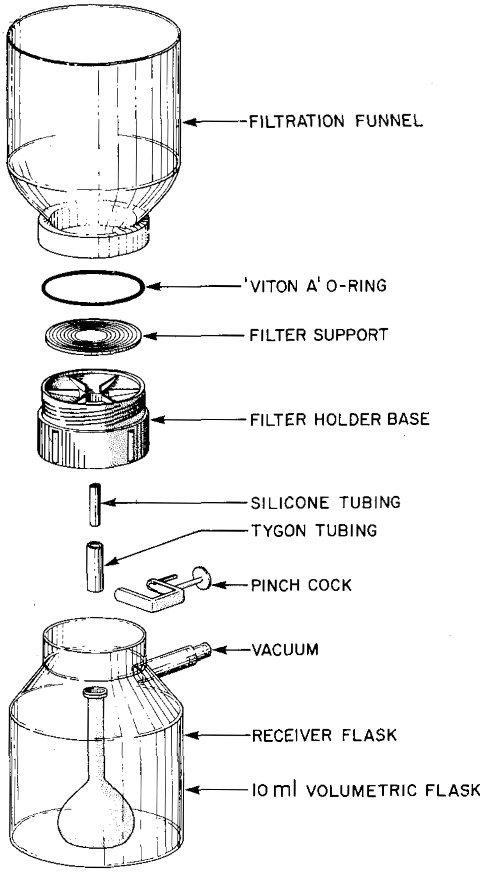

FIGURE 1 Apparatus for acetic extraction.

Reagents and standard solutions

Deionized reverse osmosis water was used throughout.

Acetic acid 25% v/v used in leaching was prepared from J. T. Baker Ultrex® grade glacial acetic acid. Ultrex grade HF 48%, HCl 37%, HNO_3 70% and Fisher ACS H_3BO_3 crystals were used in decompositions.

Standard solutions were diluted from BDH Chemicals 1000 ppm stock solutions in matrices corresponding to sample solutions (HOAc or HF decomposition matrix).

To ensure the relative accuracy of the method, several reference materials such as National Research Council of Canada estuarine sediments BCSS-1, MESS-1 and United States Geological Survey marine mud MAG-1 were analysed along with the samples.

25% acetic acid extraction

The sample filter is centered and laid flat on the moistened filter support. The filtration funnel is then screwed on tightly to the base and the pinchcock is tightened over the tygon sleeve. The filter holder base is then attached to the receiver flask and 5 ml of 25% acetic acid is placed in the funnel. The funnel is covered and let stand for 24 hours. After 24 hours the pinchcock is quickly opened, the tygon sleeve is removed and the silicon tubing inserted into a 10 ml volumetric flask placed in the receiver flask. No problems were encountered with the loss of acetic acid solution from the tubing before its insertion into the flask unless the filter was pierced or badly seated on the support.

Vacuum is then applied to the receiver flask and after all the acetic acid has been filtered into the 10 ml flask, the filter is washed twice with 2 ml of H_2O. After the final wash the funnel is removed, the filter is transferred into a Petri dish for drying at 60°C, and the rest of the filtrate remaining trapped in the filter holder is drawn by vacuum into the flask. The flask is made to the volume of 10 ml with H_2O and the solution is transferred into a polypropylene bottle and stored for AAS analyses. Nuclepore filter blanks are treated in the same manner. The dried filters containing the residual matter are then decomposed with HF/aqua regia acids.

Hydrofluoric acid—aqua regia decomposition

The decomposition of SPM samples on Nuclepore filters has been previously described by Rantala and Loring.[4] Briefly the method is as follows: The entire weighed filter is placed into the Teflon decomposition vessel, 1 ml of aqua regia and 1 ml of HF are added and the vessel is immersed in a boiling water bath for 1 hour. After cooling, the solution is transferred to a 25 ml polypropylene volumetric flask containing 0.93 g of H_3BO_3 and 5 ml of H_2O. The vessel is rinsed several times with small volumes of H_2O and the washings are added to the flask. The flask is shaken and made up to 25 ml with H_2O. The solutions are stored in polypropylene bottles for AAS analyses.

ATOMIC ABSORPTION ANALYSES

A Perkin-Elmer 303 spectrophotometer equipped with a 3-slot burner head and a Texas Instruments Servo Riter II strip chart recorder was used in the flame determinations of Cu and Zn. In the graphite furnace determinations of Cd, Pb, Cu and Zn a Perkin-Elmer HGA-500 graphite furnace was used with a model 306 spectrophotometer equipped with a deuterium background corrector, a model 056 strip chart recorder, an EDL power supply and electrodeless discharge lamps for Cd and Pb. Samples of 20 μl were injected into the furnace with a Perkin-Elmer AS-1 autosampler.

Standard uncoated graphite tubes were used. L'vov platforms were made from the grooved ends of the tube as described by Hinderberger *et al.*[5] All Cd, Pb and Zn furnace determinations were carried out by using the platform. Suppression of the absorption signals of Cd and Pb (as previously observed by us for Cd in a fluoboric-boric acid matrix without a platform[6]) was not observed in the present experiments when the platform was used. Other workers have observed a similar reduction of interferences in Cd and Pb determinations using the platform[5,7].

Since the relative accuracy of the determinations was found to be good for the total sample (±10%) from the use of reference materials, no matrix modifiers were used and all the results were derived from the calibration curves without standard additions. The maximum power (zero ramp) heating mode of the HGA-500 was used during the atomization in all the determinations. This permits atomization at a lower temperature than does the normal mode and combined with the platform results in significantly increased tube life. Copper determinations were carried out without a platform due to the relatively high temperature required for the atomization.

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

The furnace controller programs used are shown in Table I. In addition two other steps were used. The residual matrix was removed by a 3 sec firing at 2700°C and the platform was cooled 15 sec.at 20°C before the next sample was introduced. It was also necessary to lower the atomization temperature for cadmium from 1600°C in the H_3BO_3 matrix to 1100°C in the acetic acid matrix. Internal argon flow was reduced to 50 ml/min during atomization. The detection limit (i.e. the concentration of analytes giving absorption signals twice that of the filter blank) were found to be Cd 0.1 μg/1, Cu 1 μg/1, Pb 2 μg/1, Zn 2.5 μg/1 in a solution for 20 μl samples. In practical terms this would mean that 0.5 μg/g Cd, 5 μg/g Cu, 10 μg/g Pb, 13 μg/g Zn in the acetic acid extractable and 1.3 μg/g Cd, 13 μg/g Cu, 25 μg/g Pb and 31 μg/g Zn in the residual fraction could be detected in 2 mg samples of SPM using 20 μl aliquots. Except for residual Cd and Pb these levels are lower than generally found in SPM.

TABLE I

Furnace program HGA-500

	Dry °C	Char °C	Atomize °C
Cd	270	400	1100 HOAc 1600 H_3BO_3
Pb	270	550	1800
Zn	270	550	1600
Cu	120	900	2100
Ramp(s)	10	20	0
Hold(s)	20	20	3

RESULTS AND DISCUSSION

To evaluate the efficiency of the acetic acid extraction, three SPM samples (2.76, 17.2, 84.2 mg) were each extracted sequentially three times with 25% acetic acid. The sum of the three extractions is assumed to represent the total extractable metal concentration. The residual matter remaining after the third extraction was decomposed with HF and agua regia to obtain the residual metal concentration.

The results in Table II show that on the average 76.4–92.0% of the

TABLE II

Sequential 25% acetic acid extractions of Cd, Cu, Pb and Zn.

	SPM	μg/g Extracted				% Extracted			μg/g	μg/g	Extractable
	(mg)	(1)	(2)	(3)	T	(1)	(2)	(3)	Residual	Total SPM	% of Total
Cd	2.76	2.39	0.31	[a]ND	2.70	88.5	11.5	—	[a]ND	—	—
	17.2	0.99	0.09	0.04	1.12	88.4	8.0	3.6	0.13	1.25	89.6
	84.2	1.02	0.08	0.04	1.14	89.5	7.0	3.5	0.11	1.25	91.2
MEAN		1.47	0.16	0.04	1.65	88.8	8.8	3.6	0.12	1.25	90.4
Cu	2.76	225	22	10	257	87.6	8.5	3.9	74	331	77.6
	17.2	262	31	10	303	86.5	10.2	3.3	83	386	78.5
	84.2	264	54	18	336	78.6	16.1	5.3	94	430	78.1
MEAN		250	36	13	299	84.2	11.6	4.2	84	382	78.1
Pb	2.76	301	33	13	347	86.7	9.5	3.8	[a]ND	—	—
	17.2	180	35	13	228	78.9	15.4	5.7	49	277	82.3
	84.2	107	41	20	168	63.7	24.4	11.9	70	238	70.6
MEAN		196	36	15	247	76.4	16.4	7.1	60	258	76.5
Zn	2.76	331	12	[a]ND	343	96.5	3.5	—	159	502	68.3
	17.2	328	28	9	365	89.9	7.7	2.4	141	506	72.1
	84.2	315	29	8	352	89.5	8.2	2.3	146	498	70.7
MEAN		325	23	9	353	92.0	6.5	2.4	149	502	70.4

[a] Not Detected.

metals are removed with the initial extraction. The order of the removal is shown to be Zn > Cd > Cu > Pb. This order may vary depending on geochemical characteristics of SPM.

The potentially bioavailable acetic acid extractable metal concentrations are 70.4–90.4% of the total metal concentrations. The most available metal in these samples is Cd (90.4%). These high weak acid extractable metal percentages reflect the ability of SPM to adsorb metals from solution making a large fraction of the total metal potentially available to biota that might ingest the particles. Although this is generally true, in some areas the metal composition of SPM can be due to mine wastes or other sources rather than being adsorbed from solution. In such cases the potentially bioavailable proportions may be quite different. For example, in a Greenland fjord receiving mine waste, it was found that 98% of the total lead but only 8% of the total cadmium were extracted by acetic acid.[8]

When only the total metal concentration is of interest and the sample size is >2 mg, one SPM filter is decomposed for the analysis. Often however, the SPM concentration in sea water can be quite low (<1 mg/l) and the filtration time available between sampling stations may also be short for filtering large volumes. Therefore we filter our samples in triplicate and decompose duplicate filters together when the weight of SPM is <2 mg for one filter. Contamination from the Nuclepore filters does not generally present a problem. Several workers have found their total trace element concentration to be relatively low[9,10] and the filter membranes are not dissolved during the decomposition.

In the decomposition of two sample filters we used the same volume (2 ml) of acids as for one filter. To confirm the efficiency of the decomposition with two filters a second decomposition was carried out and iron, which is easily detectable was determined in both decompositions. The results showed that >97% of the total Fe was removed by the first decomposition. It may be possible to decompose more than two filters when required.

CONCLUSION

In this paper we have demonstrated how it is possible to partition and determine the heavy metals Cd, Cu, Pb and Zn without preconcentration, in small samples of estuarine marine SPM. Such data have proven valuable in assessing the potential availability of the heavy metals to biota and locating the pathways and sources of contamination.[1]

It may also be possible to use the leaching apparatus with other extractants in carrying out sequential extractions of SPM.

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