In: Analytical Techniques in Environmental Chemistry
Ed.By J. Albaiges, Pergamon Press, Oxford, New York, 1980

Extraction of Heavy Metals from Marine Sediments for Analysis by Atomic Absorption Spectrometry - Some Factors Affecting Extraction Efficiency

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ABSTRACT

The acid extraction of heavy metals from marine sediments in closed vessels for subsequent analysis by atomic absorption spectrometry was investigated, with particular attention given to the effect on extraction efficiency of the composition of the acid mixture for sediments of different composition as well as amount of sample digested. It was found that the composition of the acid mixture used in the digestion has an important effect on the concentration of metals found. Using an acid mixture determined to be most efficient for a variety of sediment types, samples taken by grab and core samplers along the Turkish Eastern Mediterranean coast were analyzed for up to seven selected heavy metals.

KEY WORDS: Sediment analysis, heavy metals, acid extraction, atomic absorption.

INTRODUCTION

The analysis of marine sediments is an important area of environmental analytical chemistry. Heavy metals, in particular, have gained importance recently due to their known detrimental environmental effects. It is thus important to study the distribution of heavy metals in marine sediments, but for this a reliable analytical method is needed.

An important technique for the analysis of metals in a variety of environmental samples is atomic absorption spectrometry. For the analysis of solid samples such as sediment, a dissolution step must precede the analysis step as solutions are most easily analyzed by atomic absorption.

Solid samples are commonly digested with acid in open or closed vessels at room or elevated temperatures. The acid or acid mixture must be able to effectively decompose both the organic and siliceous material of the sediment or be able to efficiently extract the metals. For this purpose five mineral acids, viz., HCl, HNO_3, H_2SO_4, $HClO_4$ and particularly HF, have been used by many workers either singley or in a variety of combinations, employing open or closed digestion systems.

Bernas (1968) pioneered the bomb decomposition of solid geological samples using a mixture of aqua regia and HF to dissolve silicate materials. Omang and Paus suggested a mixture of nitric and hydrofluoric acids for the digestion of geological materials in the bomb-type closed vessel (1971). Agemian and Chau demonstrated the advantages of digesting sediments in decomposition bombs when total extractable metal content, excluding mercury, is to be determined (1975). They recommended a mixture of $HF-HNO_3-HClO_4$. This mixture used with the bomb digestion technique was more efficient than any type of cold or hot extraction for a variety of different types of sediment. Other acid mixtures were not evaluated.

As the bomb technique is rapidly becoming widely-used for the decomposition and dissolution of various types of environmental samples, a study of the relative extraction efficiency of various acid mixtures with this technique, as well as other parameters affecting the digestion, would be valuable. In this study several commonly-used mineral acids and mixtures of the acids in various proportions were evaluated for their ability to extract several heavy metals from marine sediments ranging from sand to silt in nature and differing in their organic carbon contents.

Using the digestion conditions determined to be most efficient in general for a variety of different types of sediment, several samples of coastal and shelf sediments from the Mediterranean were analyzed for copper, iron, zinc, lead, manganese, chromium and nickel.

MATERIALS AND METHODS

Sample Collection and Preservation

Shore sediment samples were collected with a "VanVeen" type grab sampler. Continental shelf samples were collected with a "Shipek" grab sampler and a piston core sampler. The specimens were carefully removed from the inner portion of the samplers to avoid contamination; in the case of core samples, only the portion near the tip of the core was analyzed. All samples were sealed in plastic bags and stored at -30°.

Digestion of Samples

For analysis the wet samples were dried at 100°; the dried samples were then ground to a fine powder which was passed through a 70 mesh (0.2 mm) sieve. Digestions were carried out in PTFE-lined high pressure bomb-type decomposition vessels. About 50 mg of dried sample was digested with various acids at 140° for 4 hours. The digested samples were diluted to 50 ml with distilled-deionized water. When HF was used in the digestion mixture, 0.8 g boric acid per ml HF was added to the digested mixture to dissolve metal fluorides.

Analytical Procedures

The digested, diluted samples were analyzed by directly aspirating the solutions into an air-acetylene flame of the atomic absorption spectrophotometer. For zinc the burner head was rotated approximately 30° to the light path to reduce sensitivity. For iron, chromium and manganese less-sensitive absorption lines were used. The standard-addition method was used in all cases for calibration.

Organic Matter Determination

The organic matter content was determined by the chromic acid method (Olausson, 1975). To about 0.4 g of powdered sediment 10 ml of 1 N dichromate solution and 20 ml concentrated sulfuric acid are added carefully and the flask mixed gently for 1 minute. After 20-30 min. reaction period the solution is diluted to 200 ml with distilled water and 10 ml concentrated phosphoric acid. 0.2 g NaF and 1 ml diphenylamine indicator are added. The sample solution is then back titrated with 0.4 N ferrous ammonium sulfate.

RESULTS AND DISCUSSION

The five mineral acids in up to 15 different combinations were evaluated as extracting agents. In general it was observed that acids used singly were not as effective as mixtures. Sulfuric acid was a particularly poor extracting agent. Perchloric was the most efficient acid when used singly. To completely dissolve the sediments, HF was required. However, it was found that mixtures which did not contain HF, and thus did not result in complete sample dissolution were also effective.

In general it can be concluded that mixtures of HNO_3:$HClO_4$:HF are the best among all mixtures evaluated for a variety of sediment types. $HClO_4$: HCl mixtures which are also quite effective can be used when it is not desired to use HF due to the introduction of impurities from the boric acid treatment.

The importance of the acid used for digestion can be better understood from the data in Table 1 where the percent relative standard deviations among acids for three different types of sediment are presented. It is seen that for the sand and clay sediments, type of extracting agent used is quite important because of the wide variations observed among acids and mixtures. In the case of the muddy sediment, the choice of acid is less critical. These data demonstrate the importance of the nature of the sediment in determining the optimum extracting agent. The mechanism of incorporation of metals in sediments of differing chemical composition and physical character is obviously of prime importance, but is not well-understood and was beyond the scope of the present investigation.

When using the bomb-type closed vessels to digest sediment samples, the size of the sample digested may have an effect on the concentration of metal found, as seen in Table 2. The concentrations of nickel, chromium and lead appear to decrease with increasing weight of sample digested. The digestion period was kept constant at 4 hours for these experiments. A longer period would perhaps minimize the differences. 50 mg was chosen as the best compromise weight which allowed the metals to be detected by flame atomic absorption while at the same time leading to high extraction efficiencies.

With the optimum extraction conditions established, a study of the levels of some trace metals in a number of Mediterranean coastal and continental shelf sediments was carried out. The analytical results are presented in Tables 3 and 4.

TABLE 1. Relative Standard Deviations of Average Results of Three Types of Sediment Using Different Acid Mixtures

Sample	Organic Content(%)	Fe	Mn	Pb	Cu	Zn	Ni
Sand	1.03	15.9	22.4	-	-	34.1	-
Black mud	1.76	2.5	10.1	7.4	6.2	3.4	4.5
Clay	4.49	14.0	6.1	-	-	14.8	11.6

TABLE 2. Effect of Weight of Sample Used for Digestion on Concentration of Metal Found (µg/g).

Sample weight (g)	Fe	Mn	Zn	Cu	Cr	Pb	Ni
0.025	40185	413	587	149	628	418	391
0.050	39685	418	595	142	585	353	356
0.075	39835	422	560	146	512	345	327
0.100	40560	432	598	146	483	286	324
0.150	39270	427	586	153	479	271	318
0.200	38790	423	586	135	498	252	308
% Stand. dev.	1.6	1.6	2.3	4.3	11.6	19.4	7.1

TABLE 3. Average Trace Metal Concentration in Coastal Sediments (µg/g)

Location	Type	Fe	Mn	Zn	Cu	Pb	Cr	Ni
Ovacık	Sand	4247	170	16.9	-	-	-	-
	Sand	2987	135	18.9	-	-	-	-
	Sand	2761	115	16.5	-	-	-	-
Göksu Delta	Sand	24460	434	48.9	21.1	130	-	169
	Clay	29640	383	49.4	24.7	141	-	79
	Clay	33020	562	55.3	36.3	103	-	131
	Clay	30930	470	46.4	32.2	172	-	139
Limonlu	Mud	39700	787	62.8	32.5	53	594	556
	Mud	44400	715	74.5	33.3	55	535	480
	Mud	45100	742	72.7	37.2	63	534	477
	Sand	42700	784	47.4	23.7	-	-	332
Mersin Harbor	Mud	41730	411	483.0	368.0	280	-	294
	Mud	41610	415	406.0	112.0	155	-	325
	Mud	41100	612	69.0	25.0	93	-	343
	Mud	27320	389	44.0	24.0	46	-	104

TABLE 4. Trace Metal Concentration in Shelf Sediments (µg/g)

Type	Water depth(m)	Fe	Mn	Zn	Ni	Cu	Cr
Grab	380	39054	844	63.1	309	33.2	289
Corer	558 (3.1)#	38840	765	64.6	277	33.7	277
Grab	558	44634	1493	69.0	217	50.2	161
Corer	641 (2.4)	36853	819	81.4	247	33.1	225
Corer	450 (1.9)	38793	687	62.8	244	33.3	260
Grab	363	39216	717	75.6	277	22.5	298
Grab	1019	48180	1938	72.2	206	52.1	151
Corer	848 (1.7)	40541	990	63.5	332	29.9	305
Grab	151	42357	1499	75.4	264	42.3	246
Grab	294	41497	3335	71.8	239	46.8	198
Corer	198 (1.8)	42377	741	67.0	271	41.9	229
Corer	371 (3.0)	38198	857	54.2	319	34.5	344

\# Number in parenthesis indicates length of core

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