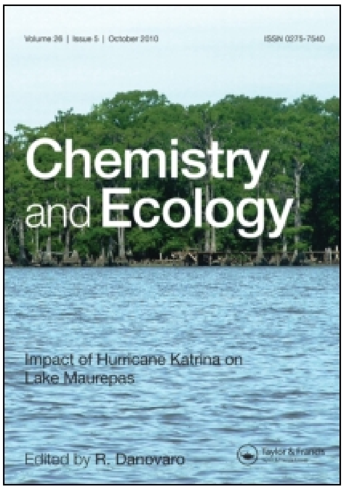

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Total and "Selective" Extraction Methods for Trace Metals in Marine Sediment Reference Samples (Mess-1, NBS 1646)

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Total and "Selective" Extraction Methods for Trace Metals in Marine Sediment Reference Samples (Mess-1, NBS 1646)

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Trace metals (Cd, Cr, Cu, Mn, Pb and Zn) and Fe were analyzed in two sediment reference samples (NBS 1646, MESS-1) with AAS fitted with graphite furnace, using five different (three total and two selective) extraction procedures.

The comparison of the total digestion methods (hot strong acids) with reference materials gave good results for almost all of them, and the "teflon bomb" was preferred for its rapidity and ease of operation. Some non-referenced data on total and organic carbon, total nitrogen and minerals are given. The two selective leaching extractions (nitric and cold hydrochloric) were also compared with reference values.

The use of certified reference materials (CRM) for environmental chemistry is recommended, together with the determination of organic matter and fundamental mineralogical composition.

KEY WORDS Extraction; Total; Selective

INTRODUCTION

Most of the interest for environmental geologists is in metal analysis and obtaining good data by rapid methods (Adams *et al.*, 1980; Casetta *et al.*, 1983) and in distinguishing, if possible, the natural from the anthropogenic level of the analyzed elements.

The analytical problem with environmental sediment samples is even more complicated due to the different possible binding metal sites within the sediment (Legret *et al.*, 1983; Trefry and Metz, 1984).

Recently MacDonald and O'Brien (1985) discussed the value of certified reference materials (CRM) for environmental chemistry and Keith *et al.* (1983) recommended their incorporation in any environmental sampling program.

Different extraction methods are often proposed as "total" or "selective" ones and there is much debate among analysts as to their meaning.

With the aim of a better understanding of this problem we present a methodological study to compare three total extraction digestion methods (Shapiro and Brannok, 1962; Bernas, 1968; Langmyhr and Paus, 1968; Adams *et al.*, 1980; Legret *et al.*, 1983), using two international standards (Standard Reference Material 1646, estuarine sediment, from National Bureau of Standards (NBS) and MESS-1, marine sediment, from National Research Council of Canada).

Two "selective" leaching procedures used for environmental samples (Carmody *et al.*, 1973; Chester and Voutsinou, 1981; Guerzoni *et al.*, 1984) were also studied and compared with the reference values.

Some other sediment characteristics, like total carbon (certified for MESS-1), organic carbon, nitrogen and mineral composition were analyzed and are presented as non certified elements.

EXPERIMENTAL

Apparatus

Two Perkin Elmer mod. 603 and 5000 atomic absorption spectrophotometers, each fitted with an HGA-500 graphite furnace and deuterium background corrector, were used throughout this work.

L'Vov pyrolytic graphite platforms were used in conjunction with normal and pyrolytic graphite coated tubes. The latter were indispensable for Pb and Cd determinations. Hollow cathode lamps used for all the elements were operated under the recommended conditions. Total and organic C and N were analyzed by a Carlo Erba mod. 1106 CHN/OS analyzer.

The minerals composition was identified with X-ray diffractometry analysis (Philips, mod. PW 1390).

Reagents and materials

Standard solutions of the elements were prepared by dissolution of their salts (Carlo Erba) to produce 1000 $\mathrm{mgl^{-1}}$ stocks. For preparation and dilution of the samples double distilled filtered water (DDW, Milli-Q Water System) was used. Boric acid and idrazine sulfate were high purity standard (Carlo Erba). Mineral acids were ultra-pure quality from Prolabo. Ammonium dihydrogen phosphate (0.2%) and magnesium nitrate (0.05%) were used as matrix modification reagents for Pb and Cd.

Procedures

All sample preparations were done in a clean laboratory. Sediment samples were dried to constant weight at 105°C and 0.5 g weighed out for each analysis. All the following procedures (A to E) were done in five replicates and a blank was run omitting the samples each time.

(*A*) "*Teflon bomb*". The sample was ground at 150–200 mesh, placed in a 35 ml teflon crucible and attacked with a solution of 6 ml of HF and 1 ml of "aqua regia" (HNO_3–HCl, 1:3, v/v). The "bombs" are heated in an oven at 170°C for 2 hours and cooled with tap water. The content is transferred to a 125 ml polyethylene beaker and 25 ml of warm DDW and 2 g of boric acid are added, to buffer HF and solubilize the other salts (Farmer and Gibson, 1981). The solution is shaken until completely clear, allowed to reach room temperature and diluted to 50 ml in volumetric flasks. This procedure was modified from Bernas (1968) and Langmyhr and Paus (1968).

(*B*) "*Solution B*". The sample was weighed in a 30 ml teflon crucible and leached with 15 ml of the following solution: 450 ml of concentrated HF, 165 ml concentrated H_2SO_4 and 40 ml concentrated HNO_3. The crucibles were put on a hot plate (160°C) for 12 hours; after cooling at room temperature, 3 ml of concentrated HNO_3 were added with approximately 20 ml of DDW, to decompose the sulfate. The content was transferred to a pyrex beaker on a hot plate to dry and a few drops of a mixture (1:1) of HNO_3 and $HClO_4$ were added to eliminate the organic matter. Finally 25 ml of DDW, 4 ml of conc. HNO_3 and 1 ml of idrazine sulfate (0.2 g in 100 ml of water) were added to avoid precipitation of Mn compounds, the solution boiled until it was clear, and then diluted to a final volume of 50 ml. The digestion method was modified from Shapiro and Brannock (1962).

(*C*) "*Minerox*". Ten ml of concentrated HNO_3 and 10 ml of concentrated HCl were added to 0.5 g of dried sample, as previously described. The samples were placed in 200 ml pyrex tubes on hot plates (Minerox) at 95°C for a digestion period of 5 hours. A minimum volume of double distilled water was added periodically to the sample to rinse the sides of the tubes and to avoid dryness. After cooling the samples were diluted with double distilled water and filtered through n. 42 Whatman filter paper into 50 ml volumetric flask (Anderson 1974; Adams *et al.*, 1980).

(*D*) "*Hot nitric*". Fifteen ml of 8N-HNO_3 were used to leach the samples in a 50 ml Pyrex beaker on a hot plate (90°C) for 30 minutes. Then the solution was suction filtered (Whatman n. 42) and the beaker sides were rinsed with DDW to recover all the leachate. The filtrate was diluted to 50 ml with double distilled water (Carmody *et al.*, 1973; Guerzoni *et al.*, 1984).

(*E*) "*Cold hydrochloric*". The samples were placed in 100 ml wide new glass bottles, 20 ml of 1N-HCl were added (evolution of CO_2 being allowed when necessary) and the bottles shaken mechanically for approximately 16 hours. The solution was allowed to stand for a few minutes, then suction filtered, and the filtrates were diluted to 50 ml volumetric flasks with double distilled water (Chester and Voutsinou, 1981).

RESULTS AND DISCUSSION

Total digestion

The A, B and C procedures were checked as total digestion methods for the studied metals. Results of the analysis of the marine sediment reference materials MESS-1 and NBS are presented in Table I.

Very small differences were observed between the "teflon bomb" and "sol B" methods and the results show good agreement between reference values and graphite furnace data for all elements, with the exception of Fe in NBS and Cr in MESS-1 samples, probably due to the difference in mineral composition. The "teflon bomb" method seemed to be more suitable for the total digestion extraction since it showed less variability, possibly due to minimal manipulation.

Method C ("Minerox") gave total recovery for Cd, Pb and Cu,

TABLE I

Analytical data of the total digestion procedures, compared to the certified reference values. Values are % and ppm on a dry weight basis

NBS-1646 Standard

Element	"Teflon bomb"[a]	"Sol. B"[a]	"MINEROX"[a]	Reference value[c]
Fe (%)	3.61 ± 0.03	3.57 ± 0.03	2.98 ± 0.06	3.35 ± 0.10
Mn (ppm)	386 ± 8	381 ± 3	285 ± 3	375 ± 20
Cd	0.40 ± 0.05	0.42 ± 0.01	0.33 ± 0.02	0.36 ± 0.07
Pb	28.1 ± 3.1	24.4 ± 2.2	28.1 ± 2.4	28.2 ± 1.8
Zn	140 ± 7	143 ± 3	168 ± 9	138 ± 6
Cu	18.0 ± 1.7	18.1 ± 3.4	17.4 ± 1.1	18.0 ± 3.0
Cr	75 ± 8	75 ± 1	48 ± 1	76 ± 3

MESS-1 Standard

Element	"Teflon bomb"[a]	"Sol. B"[a]	"MINEROX"[a]	Reference value[b]
Fe (%)	3.16 ± 0.19	3.27 ± 0.03	2.56 ± 0.12	3.05 ± 0.17
Mn (ppm)	535 ± 11	529 ± 5	371 ± 5	513 ± 25
Cd	0.56 ± 0.02	0.57 ± 0.01	0.51 ± 0.04	0.59 ± 0.10
Pb	29.9 ± 4.9	33.0 ± 4.3	35.3 ± 5.8	34.0 ± 6.1
Zn	190 ± 4	194 ± 2	167 ± 32	191 ± 17
Cu	24.1 ± 1.3	26.9 ± 1.0	23.1 ± 1.9	25.1 ± 3.8
Cr	59 ± 5	64 ± 5	35 ± 1	71 ± 11

[a] Precision expressed as standard deviation of the mean ($n = 5$).

[b] Precision expressed as 95% tolerance limits for an individual subsample (Berman, 1981).

[c] The estimated uncertainty for an element is based on judgement and represents an evaluation of the combined effects of method imprecision, possible systematic errors among methods and material variability for samples 500 mg or more.

whilst Fe, Mn, and Cr were underestimated, in contrast to the findings of Adams *et al.* (1980). The lack of complete dissolution of some minerals can also explain the low yield of Cr, probably reflecting the chromite content in the studied material. Zn behaved differently: in the NBS standard it was overestimated and showed low variability, whilst in MESS sample it gave different values, from under- to over-estimates, with an exceptionally high value for one subsample erroneously taken to dryness, probably due to Zn leached from Pyrex.

Total carbon was run directly on the dried sample in triplicate and the data were in perfect agreement with the certified value.

Non-certified elements

In Table II, total, organic and carbonate carbon and total nitrogen data are given and in Table III is shown the fundamental mineralogical composition of the reference samples.

Both sediments show very low content of carbonate C and a different content of organic C. The low N levels (non certified) are consistent with the prevailing siliceous matrix of the two samples. The carbonate component is almost absent, as shown from the chemical analysis.

These data are added to suggest that their use during metal analyses will be of interest for those laboratories working with international reference samples and certified from NBS and NRC of Canada.

TABLE II

Total, organic and carbonate carbon and total nitrogen for NBS and MESS-1 reference samples (certified reference value for MESS-1: C = 2.99 ± 0.09). All data are expressed in %, on a dry weight basis

Element	NBS-1646	MESS-1[a]
total C	1.70 ± 0.03	2.94 ± 0.03
organic C	1.53	2.66
carbonate C	0.17	0.28
total N	0.16	0.18

[a] Precision expressed as 95% tolerance limits for an individual subsample (Berman, 1981).

TABLE III
Fundamental mineralogical composition for NBS and MESS-1 reference samples, expressed as semiquantitative estimate, compared with a pure mineral mixture; data are expressed in %, on a dry weight basis

Mineral	NBS-1646	MESS-1
Quartz	35	27
Plagioclase	48	40
Muscovite/Illite	6	7
Chlorite	3	8
Kaolinite	2	4
K-feldspar	5	5
Anphiboles	1	3

Selective extractions

To focus on the environmental significance of the analyzed trace metals, many authors experiment with selective leaching extractions to dissolve the anthropogenic part of the element and to give a "quick" indication of polluted areas (Adams *et al.*, 1980; Chester and Voutsinou, 1981; Donazzolo *et al.*, 1981; Trefry and Metz, 1984).

It is beyond the aim of the present paper to discuss the environmental and bioavailability implications of all the studied extraction procedures. We show in Table IV the data of two of the most commonly used (among Italian and European laboratories: Donazzolo *et al.*, 1981; Cosma *et al.*, 1982; Guerzoni *et al.*, 1984) extraction procedures in environmental studies, compared to the total reference content.

In the rearranged Table V, the studied elements are grouped according to the percentage extraction. It is evident that both methods, as expected, dissolve the metals only partially (mean $(D) = 55\%$; mean $(E) = 25\%$), with some large differences between them. This highlights the difficulties that environmental analysts have in obtaining meaningful and comparable results and the importance of associating the total digestion procedure, the mineralogical characterization, and the organic matter content with any "selective" extraction protocol.

TABLE IV
Analytical data of the leaching extractions, compared to the certified reference values. Data given as % and ppm on a dry weight basis

NBS-1646 Standard			
Element	"8N HNO$_3$-Hot"[a]	"1N HCl-Cold"[a]	Reference value[c]
Fe (%)	2.22 ± 0.01	0.74 ± 0.01	3.35 ± 0.10
Mn (ppm)	211 ± 3	98 ± 2	375 ± 20
Cd	0.23 ± 0.04	0.10 ± 0.01	0.36 ± 0.07
Pb	11.0 ± 0.5	5.5 ± 0.2	28.2 ± 1.8
Zn	110 ± 3	84 ± 1	138 ± 6
Cu	13.4 ± 1.1	3.5 ± 0.2	18.0 ± 3.0
Cr	29 ± 1	13 ± 1	76 ± 3
MESS-1 Standard			
Element	"8N HNO$_3$-Hot"[a]	"1N HCl-Cold"[a]	Reference value[b]
Fe (%)	1.74 ± 0.04	0.35 ± 0.01	3.05 ± 0.17
Mn (ppm)	243 ± 4	71 ± 3	513 ± 25
Cd	0.35 ± 0.10	0.15 ± 0.03	0.59 ± 0.10
Pb	13.5 ± 1.0	6.9 ± 0.4	34.0 ± 6.1
Zn	172 ± 12	104 ± 2	191 ± 17
Cu	18.4 ± 3	5.9 ± 0.3	25.1 ± 3.8
Cr	15 ± 2	7 ± 1	71 ± 11

[a] Precision expressed as standard deviation of the mean ($n = 5$).

[b] Precision expressed as 95% tolerance limits for an individual subsample (Berman, 1981).

[c] The estimated uncertainty for an element is based on judgement and represents an evaluation of the combined effects of method imprecision, possible systematic errors among methods and material variability for samples 500 mg or more.

TABLE V
Rearranged values of leaching procedures, expressed as averaged percentages of total content

"8N HNO$_3$-Hot"		"1N HCl-Cold"	
Cr, Pb	20–40%	Fe, Cr	10–20%
Fe, Mn, Cd	40–70%	Mn, Cd, Pb, Cu	20–30%
Cu, Zn	70%	Zn	50%

CONCLUSIONS

Among the three methods checked for their ability to dissolve metals, the simple "teflon bomb" digestion method was preferred to the "open beaker" and "minerox" methods, as being the most suitable to recover the total content of the analyzed trace metals and because of its speed and ease of handling.

Non certified element (total nitrogen, organic carbon and minerals) determination is suggested for environmental analysts using international reference standards.

The variability in the percentage extraction of the "selective" methods indicates the difficulty in using them as indicators of the anthropogenic input of metals.

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