An evaluation of the determination of heavy metals, barium and phosphorus in sea-bed sediments

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An evaluation of the results obtained by following established procedures for collection and analysis of sea-bed sediments indicates that there is an acceptable reproducibility using nitric acid extraction and subsequent ICP-determination of Mn, Pb, Cr and P, but a somewhat lower reproducibility for Cu, Zn, Co, V and Ba. For the elements Cd and Hg determined by AAS on the same extracts, the reproducibility is poor. For Zn, Pb, Ni, Co, V, Cr and Ba, the discrepancy between the estimated and measured mean is slightly above 10%. Of the 35 samples, 1-2 samples gave Fe, Mn, Cu, Zn, Pb, Co and Hg values above the estimated maximum level, i.e. action limit, while 3-4 samples gave values above the estimated maximum level for P, Ni, V, Cr and Ba. A linear correlation is evident between the total content of Fe, Mn and P in these sediments as obtained by XRF analyis and the amount removed by nitric acid extraction, with 85±2%, 90±1% and 84±1%, respectively, being dissolved.

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Introduction

There is a controversy about the suitability of environmental parameters determined after a partial extraction in concentrated acids (e.g. HNO_3), those determined by so-called 'total' digestion in very strongly oxidising acid mixtures (e.g. $HClO_4$-HF) or non-destructive methods such as X-ray fluorescence which gives the total content. This controversy exists because there is uncertainty over the value of an analytical result reported as a partial extraction as compared to the total values enforced by pollution monitoring authorities.

The Geological Survey of Norway has collected and analysed sea-bed sediments in the Norwegian part of the Skagerrak area as part of a collaborative project which aims to assess the environmental development and status of this 12,000 km^2, offshore area located in northwestern Europe. The results of this project, entitled 'Environmental Assessment of the Skagerrak', should form an important future reference for the monitoring of contaminant input and the determination of guide-lines for the exploration of natural resources (e.g. petroleum and fishing industry) and other human activities (e.g. shipping traffic, recreation). The analytical results from this project are, as with all analytical results, subject to a certain degree of uncertainty. This paper describes the procedure for sampling the sea-bed sediments, the analytical programme specifically designed for the determination of inorganic constituents, and assesses the uncertainty associated with the reported analytical results. The results of the partial extraction of Fe, Mn and P are compared with the results obtained by XRF-analysis. All the analyses have been carried out at the analytical laboratories of the Geological Survey of Norway, which are accredited (according to EN 45001) by Norwegian Accreditation for chemical, sedimentological and mineralogical analyses under registration No. P020. Standard procedures for analytical control have been described by several authors and committees (e.g. Kateman & Pipers 1981, Montgomery 1985, Analytical Methods Committee of the Royal Society of Chemistry 1989, Gardner 1989, Mesley et al. 1991, Grimstvedt 1995.).

Methods

Sample collection

Samples were collected during the summers of 1992 and 1993 at 74 pre-determined sites located within an approximately 10 x 10 km grid covering the northern part of the Norwegian Skagerrak area (ca. 7,000 km^2). The samples were recovered from the sea-bed using a Niemestø® core sampler. This sampler forces a 63 mm diameter polyvinylchloride (PVC) pipe into the sediment. The approximate vertical penetration depth was in most cases in excess of 50 cm. When the sample core was safely placed on the ship's deck, the sediment was cut in 2 cm-thick slices, starting from the water/sediment interface. Some of the cores were shorter than 55 cm, resulting in a loss of subsamples. A total of 775 samples were collected at a 94.5% recovery rate during the 1992 and 1993 cruises. Each slice was placed in a polyethylene (PE) bag and transported in frozen condition to the laboratory. Here the samples were weighed and freeze-dried for determination of moisture content. The freeze-dried sample was rolled out while being kept inside the plastic bag before sieving through a 2 mm nylon screen. The <2 mm fraction (i.e. sand, silt and clay) was ground in an agate mill. To avoid geographical distortion caused by possible syste-

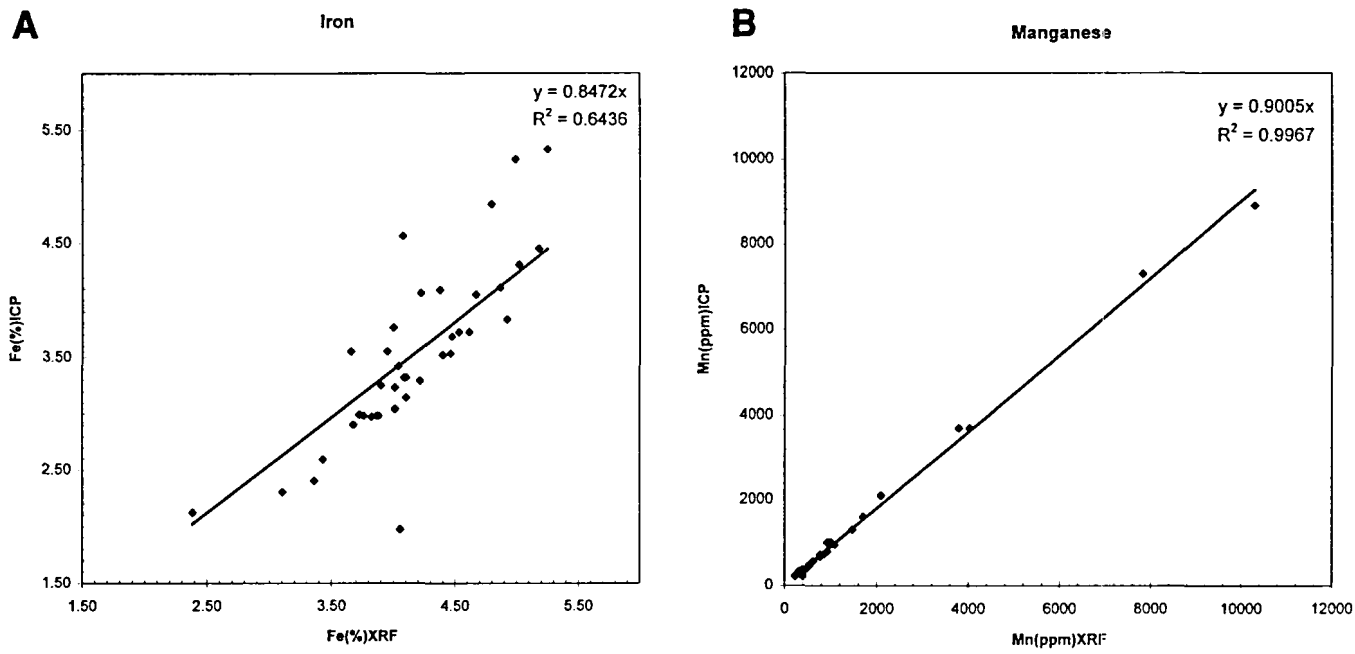

Fig. 1. The total concentrations of Fe, Mn and P determined by X-ray fluorescence (XRF) plotted against the amount extractable in boiling nitric acid (7N Ultrapure HNO3) measured by inductively coupled plasma emission spectrometry (ICP-AES).

matic analytical drift, the samples were analysed in random order. Estimates of the combined variability due to sample splitting and analysis, i.e. total reproducibility, were made by collecting and analysing 4.5% (n=35) duplicates and 1.4% (n=10) inter-year duplicates.

Extraction of samples and chemical analysis

One gram of freeze-dried sediment sample, which consists mainly of quartz, various feldspars and clay minerals, was extracted with 20 ml 7N Ultrapure HNO_3 in an airtight borosilicate bottle in an autoclave for half an hour at 120°C, according to Norwegian Standard NS 4770. After dilution with water by a factor of five, the extract was analysed for Fe, Mn, P, Cu, Zn, Pb, Ni, Co, V, Cr and Ba by inductively coupled plasma atomic emission spectrometry (using a Thermo Jarrell Ash ICAP 61 ICP-AES) and for Cd and Hg by atomic absorption spectrometry (AAS, Perkin Elmer). Instrumental precision, together with results obtained on the international, certified reference materials PACS-1 and CRM-277 are presented in Table 1 (Ødegård, 1996). The table also shows the limits of determination of the methods used. For comparison with total element content, Fe, Mn and P were determined in 38 sea-bed samples (taken at a depth of 4-6 cm below the sediment/water interface) by X-ray fluorescence (XRF, Philips PW 1480). Sample aliquots of 0.8 g material ignited at 1000°C were mixed with 5.6 g $Li_2B_4O_7$ flux and fused to a glass disk prior to analysis. This homogenises the sample material, eliminates the effects of variation in grain-size and reduces the matrix effects.

Results and discussion

The results obtained after autoclave extraction with 7N HNO_3 of the certified reference materials PACS-1 and CRM-277 are presented in Table 1. It is important to note that the certified values represent the total concentration of each element in the samples, whereas the results

Table 1. Instruments used and results obtained on certified international standards PACS-1 and CRM-277 after autoclave extraction in 7N Ultrapure HNO3. All values given in mg/kg except Fe(%).

Detection	PACS-1			CRM-277			Precision		Analytical		
	Obtained	Certified values (total)	% extractable PACS-1	Obtained values (total)	Certified	% extractable CRM-277	(n=10 PACS-1)		precision (n=10 PACS-1)		limit
Fe (%)	4.49	4.68±0.08	95.9	4.67	(4.55)	100	4.53	324ppm	4.49	1100ppm	5
Mn	298.5	470±12	63.5	1400	(1600)	87.5	302.1	1.9	298.5	5.8	0.2
P	887.4	1105±78	80.3	4000	(4100)	97.6	887.9	11.7	887.4	17.4	10
Cu	454.1	452±16	100.0	101.9	101.7±16	100	442.6	3.2	454.1	7.7	1
Zn	765.9	824±22	92.9	508.0	547±12	92.9	772.8	4.4	765.9	3.2	2
Pb	375	404±20	92.8	129.8	146±3	88.9	377.1	3.9	375.2	6.0	5
Ni	38.3	44.1±2.0	86.8	40.3	43.4±1.6	92.9	36.5	0.8	38.3	2.5	2
Co	16.2	17.5±1.1	92.6	14.4	(17)	84.7	16.0	0.2	16.2	0.4	1
V	88.2	127±5	69.4	72.1	(102)	70.7	89.4	0.6	88.2	1.6	1
Cr	55.4	113±8	49.0	138.2	192±7	72.0	55.9	0.4	55.4	0.9	1
Ba	371.4		35.1	117.9	(329))	35.8	376.3	3.0	371.2	3.2	1
Hg(CV-AAS)	n.a.	n.a.	n.a.	n.a	n.a.	n.a.	0.0016*	0.003*	n.a.	n.a.	n.a.
Cd(GF-AAS)	1.78	2.38±0.22	74.8	12.0	11.9	100	1.78	0.29	12.0	1.24	n.a.

Table 2 (a). Mean and standard deviations calculated for the absolute value of the differences between within batch duplicate samples (n=35) and the theoretically estimated (i.e. expected) statistical parameters.

Element	|d| Mean (Measured)	|d| σ (n=35)	|d| 1·128*σ (Expected mean)	Percent difference (R.D.)	|d| 2·8*σ	No.of samples |d| >2.8*σ
Fe	0.109	0.113	0.128	14.8	0.317	1
Mn	24.28	47.37	53.66	54.7	133.19	2
P	22.12	18.12	20.44	8.2	50.74	4
Cu	0.64	0.60	0.68	5.9	1.68	1
Zn	3.25	2.90	3.27	0.6	8.12	2
Pb	8.16	23.11	26.07	68.7	64.72	1
Ni	1.78	1.41	1.60	11.3	3.96	4
Co	0.58	0.50	0.57	1.8	1.41	2
V	3.90	3.28	3.70	5.4	9.17	4
Cr	2.30	1.79	2.02	13.9	5.02	3
Ba	5.30	3.44	3.88	36.6	9.63	3
Hg	0.01	0.01	0.01	0	0.02	1
Cd	0.08	0.08	0.09	11.0	0.22	1

Table 2 (b). First-order equations and the associated correlation coefficients established from the analyses of within-run duplicates (n=35) of sea-bed sediments.

Y_{Fe}	=	0.891	*	X	+	0.373	r = 0.965
Y_{Mn}	=	0.990	*	X	+	4.34	r = 0.999
Y_{P}	=	1.006	*	X	-	5.02	r = 0.923
Y_{Cu}	=	0.953	*	X	+	0.802	r = 0.901
Y_{Zn}	=	0.987	*	X	+	0.757	r = 0.852
Y_{Pb}	=	0.869	*	X	+	6.19	r = 0.897
Y_{Ni}	=	0.779	*	X	+	7.01	r = 0.794
Y_{Co}	=	0.926	*	X	+	0.695	r = 0.941
Y_{V}	=	0.992	*	X	+	0.733	r = 0.976
Y_{Cr}	=	0.899	*	X	+	4.78	r = 0.777
Y_{Ba}	=	1.04	*	X	+	3.06	r = 0.971
Y_{Hg}	=	0.958	*	X	+	0.004	r = 0.945
Y_{Cd}	=	0.439	*	X	+	0.194	r = 0.444

Table 3. First order equations and the associated correlation coefficients established from analysis of inter-year duplicate samples (n=10) of sea-bed sediments.

Y_{Fe}	=	1.28	*	X	-	0.279	r = 0.967
Y_{Mn}	=	1.05	*	X	+	6.55	r = 1,0
Y_{P}	=	0.944	*	X	-	23.5	r = 0.94
Y_{Cu}	=	0.952	*	X	+	2.35	r = 0.969
Y_{Zn}	=	1.15	*	X	+	2.66	r = 0.981
Y_{Pb}	=	1.09	*	X	-	7.08	r = 0.968
Y_{Ni}	=	1.05	*	X	+	0.733	r = 0.81
Y_{Co}	=	1.24	*	X	+	1.96	r = 0.933
Y_{V}	=	1.06	*	X	+	3.67	r = 0.99
Y_{Cr}	=	0.752	*	X	+	14.3	r = 0.712
Y_{Ba}	=	1.03	*	X	+	1.74	r = 0.92
Y_{Hg}	=	1.33	*	X	-	0.0118	r = 0.967
Y_{Cd}	=	0.515	*	X	+	0.286	r = 0.24

based on the extraction procedure used in this study (NS 4770) give the extractable or partial content. The percent extracted will obviously vary depending on element and material (e.g. 35-100% for PACS-1 and 35%-100% for CRM-277).

The analyses of the 35 duplicates (4.5% of the total number of samples collected), giving an expression of the repeatability (within-run precision) (Miller & Miller, 1988), are shown in Table 2. The basis for this presentation is taken from a report by the Analytical Methods Committee of the Royal Society of Chemistry - Statistical Sub-Committee (1995). Here the mean and standard deviation of the absolute values of the differences between each duplicate (Equation 1) is calculated and compared with the estimated (i.e. expected) mean of the absolute differences (1.128*σ) and the estimated 95th percentile (2.8*σ),

$$|d_i| = |(x_{i2} - x_{i1})| \quad \text{(Eq 1)}.$$

Assuming that the results, x_{ij}, are normally distributed, the difference between duplicates, d_i, should have a zero-centered distribution with a standard deviation of $\sqrt{2}\sigma$. In

this case, however, the absolute differences, |d|, are examined. The expected mean for |d| is 1.128σ and the 95% relevance interval would be bounded by approximately 2.8σ. In this statistical treatment, 2.8σ and 4.6σ correspond to the warning- and action-limits, respectively, in a conventional X-chart.

There is a good agreement between the expected mean (1.128*σ) and the calculated mean for all elements except for Mn, P and Ba, which show deviations of more than 30%. This probably reflects the fact that these elements occur as major elements in certain particles (e.g. grains of Mn-oxide, apatite and barite). For Fe, Ni, Cr and Cd, the deviations are above 10%. The analyses gave 1-2 values outside the estimated maximum level (i.e. 4.6σ) for Fe, Mn, Cu, Zn, Pb, Co and Hg, and 3-4 values for P, Ni, V, Cr and Ba.

Ten samples (1.4% of the total), which act as inter-year duplicates for a testing of the reproducibility (i.e. between-run precision, Miller & Miller, 1988), were selected from the samples collected in 1992 and re-analysed in 1993. The two sets of analyses from 1992 and 1993 gave the correlation coefficients shown in Table 3. The intercept is significantly offset from the origin for Mn, P, Pb and Cr, and is offset by more than one unit for Cu, Zn, Co, V and Ba. The slope varies between 0.515 (Cd) and 1.33 (Hg), both of which were determined by AAS. The correlation coefficient is greater than 0.9 for all elements except for Cd (r=0.24), Cr (r=0.71) and Ni (r=0.81).

To evaluate the extractable amount of the elements Fe, Mn and P in nitric acid, 38 samples taken from a depth of 4-6 cm below the water/sediment interface were analysed and compared with X-ray fluorescence (XRF), which gives total contents. This test showed that 85±2%, 90±1% and 84±1%, respectively, of Fe, Mn and P were dissolved with 7N HNO_3.

Conclusions

Most geological reference materials are certified for their total element content. This poses a problem when the accuracy is to be documented. The advantages of a so-called 'total' extraction are that it relates analyses to a common norm irrespective of how the contaminants are mineralogically bound. However, the convenience and low cost of elemental analyses based on partial extraction have led to the frequent use of such methods. Such methods also have many advantages and will inevitably continue to be widely used in the future (Ødegård, 1995). Advantages include lower detection limits as a result of a reduced requirement for dilution, and fewer problems with matrix interferences. For information on bioavailable elements, weak extrants will obviously be of great significance. It may also give an indication on what amount is biologically available depending on which extractant is used. The results of this study indicate that the reproducibility obtained when using nitric acid extraction is good for Fe, Cu, Zn, Ni, Co, V and Ba. For Cd and Hg determined by AAS the reproducibilty is poor. A comparison of the results of extraction by 7N HNO_3 of sea-bed sediments from the Norwegian part of the Skagerrak with the results obtained by XRF analysis of the same samples showed that around 85±2%, 90±1% and 84±1% of the total amount of Fe, Mn and P were extracted.

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