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Digests or Extracts? – Some Interesting but Conflicting Results for Three Widely Differing Polluted Sediment Samples

Iain L. Marr*, Petra Kluge, Laura Main, Vincent Margerin, and Cyrille Lescop

Chemistry Department, The University, Old Aberdeen, Scotland, AB 9 2UE, U.K.

Abstract. Three sets of samples have been investigated in some detail. One set is from a river polluted by mine workings, containing substantial levels of Fe, Mn,Cu, Zn and Ni with traces of many other metals. The second set consists of typical estuarine sediments contaminated from a wide range of industrial sources, and the third set consists of oily drilling cuttings from the sea bottom in the vicinity of a North Sea oil production platform.

These samples have been subjected to treatment 1) with EDTA at two different pH's (*extracts*) 2) with HNO_3/H_2O_2 3) with HNO_3/HCl and 4) with $HNO_3/HCl/HF$ (*digests*). EDTA recoveries, compared to *aqua regia* digests, are often very reproducible, not dependent on pH, and usually significantly low. Nitric/peroxide and *aqua regia* digests often give very close results suggesting that these are meaningful values indicating the maximum levels of polluting metals in the sediments. However, the triple acid digest with HF does sometimes give higher values (and reasonable agreement for CRM's such as MESS-1) but with poorer reproducibility.

Key words: sample digestion, microwave, sediments, trace metals.

The analysis of sediment samples for heavy metals is called for in connection with many different environmental problems. In the case of the North Sea oil fields, the analyses are required by law, as part of an on-going programme of monitoring of the North Sea. In the case of some rivers in the south of Spain the interest is the starting point for discussions on possible remediation programmes. In both cases, the real concern is the possible effect of heavy metals in the sediments on any life in the sediments or in the water above them. While soil scientists have for many years made use of EDTA extraction at pH 7 to give a picture of the levels of *available* heavy metals, available, that is, to plants growing in the soil, it seems that nowadays we are being asked to use the strongest possible forms of attack to determine heavy metals in North Sea sediments, and we should ask whether this is really desirable or sensible.

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* To whom correspondence should be addressed

It is probably true that the action of exudates from plant roots on soil minerals can be simulated by an EDTA solution, and it is possible that some soils at least will buffer the extracts to a neutral pH. On the other hand, the stomach fluids in animals can be much more acidic, and this might justify the choice of a stronger acid attack than with buffered EDTA, to assess the levels of metals which might be available to fish and shellfish. But is the combination of *aqua regia* with hydrofluoric acid a reasonable substitute for animal digestive fluids?

Ostwald, who many years ago coined the term "ripening of crystalline precipitates" to account for marked decreases in reactivity with time after initial precipitation, was already pointing us in one significant direction. Thus, freshly precipitated barium sulphate will, as the solubility product allows us to predict, dissolve quite readily in EDTA at pH 10, while the well aged material will be slow to dissolve, and geological material will be remarkably inert. If such a material is so inert in the presence of strong acid attack, is it also inert towards animal digestive fluids? The medical profession must have assumed so, before they would have decided to administer suspensions of barium sulphate to patients in preparation for X-radiography of the stomach. Thus we see that consideration must be paid to both thermodynamic and kinetic stabilities of the solid phases in sediments, and both of these from the point of view of both biological systems and chemical laboratory simulations.

Three very different sets of sediment samples have been the subject of investigation in our laboratories for some time, with the aim of enabling us to make a better choice of methods of sample attack prior to quantification of heavy metals. Are we really trying to determine *total* levels of metals, or is it more informative to try to assess levels of extractable metals, or, if we know how to, of available metals?

Sequential extraction schemes have been proposed by Tessier [1], and by Förstner [2], and compared by Ure et al. [3], aimed at distinguishing metals according to the nature of their binding – bound in the carbonate fraction of a soil, or adsorbed to the oxidised forms of manganese and iron, or complexed with organic ligands, or precipitated as sparingly sulphides. A more recent approach has been advocated by Thomas et al. involving only three steps in a sequential extraction, and tested on a river sediment reference material in an inter-laboratory comparison [4].

Selective extraction of metals in soils is an accepted procedure, long used to assess the levels of trace elements not just present in the soil, but likely to be available to plants. An EDTA solution buffered to pH 7 is recommended [5].

But it is still more usual to be asked for total levels of metals in sediments, and discussion has focussed on the choice of acid digest which this would require, as an alternative to a fusion, e.g. with sodium carbonate or lithium metaborate. Attack with *aqua regia* or with nitric acid and hydrogen peroxide is widely used to bring the greater part of the metals in a sample into solution [6], accepting that a part will remain locked in the lattice of insoluble silicate minerals. However, Loring and Rantala [7] have expressed their views very clearly that an acid attack including the use of hydrofluoric acid is the only logical choice since (a) this is the only acid attack which dissolves the silicate minerals, (b) the accuracy of a proposed method can be checked on certified reference materials only when it achieves total analysis and (c) data will be free from operationally defined bias only when total dissolution is achieved. Point (b) has been answered by Thomas et al. by suggesting that their reference material be certified for certain selective extraction procedures [4]. This paper addresses point (c) and will show that partial extraction procedures can be sufficiently robust and at the same time deliver useful information relating to the nature of the samples, and makes a case for *not* using the three-acid combination with HF for sample attack.

Experimental

The Background to the Samples

The sets of sediment samples came from three very different sources, and thus present us with a range of heavy metals bound in different ways and accompanied by different combinations of other species. But in all three sets, we find both "geological" material, and more recently deposited material of anthropogenic origin.

The Estuary of the River Clyde, in Scotland – an Estuarine Sediment

This carries a burden of pollution from the large industrial city of Glasgow, and also a substantial amount of alluvial deposit carried down by the river over a long period of time. These sediments have been equilibrated with seawater, and show marked changes in composition with increasing depth.

The River Odiel in South-West Spain – a Rivurine Sediment

This river, and the neighbouring Rio Tinto, carry run-off from tips of minerals left over from the flotation treatment of copper sulphide ores. Aerial (and possibly bacterial) oxidation of the residual sulphides results in the formation of sulphuric acid, which then in turn leaches many metals from the low-grade ores. The stretches of this river just below the mines are very acidic (pH 2.5) and carry very substantial burdens of metal ions in solution. As the waters further down stream are buffered on mixing with other streams, the pH rises and the metals are precipitated, giving contaminated, finely divided, sediments of relatively recent origin.

The Bed of the North Sea – a Marine Sediment of Drilling Cuttings

The samples were collected in the vicinity of an oil production platform, where recent deposits have built up from the discharged rock cuttings resulting from drilling operations, cuttings which are also mixed with several finely ground minerals used to constitute the drilling mud. A major mud component is crude barytes, containing some 60–80% of barium sulphate contaminated with a number of other heavy metals. Other mud minerals are calcite and clays such bentonite.

Sample Preparation

All sediment samples were air-dried at 35 °C for two days, sieved to remove particles >1 mm, and ball milled to pass through a <63 μm sieve. Though the drilling cuttings contained a high level (typically 10% w/w) of hydrocarbons (from the drilling fluids) once ball-milled they felt quite dry and could be handled easily, due to the large specific surface area.

Sample Digestion Procedures

Microwave digestion with aqua regia: Portions of ground sample (1 g) were treated with 10.0 ml of *aqua regia* in closed 120-ml PTFE vessels. Batches of twelve vessels were heated in a CEM model MDS-81D microwave oven, for 30 minutes at 25% power and then for 50 minutes at 50% power. This programme was arrived at after an optimisation investigation, and was adopted because it gave the same results for sample weights of 0.5 g as for 1 g. After cooling, the vessels were opened, centrifuged to throw residual solids to the bottom, and the liquid phases decanted and made up in 25-ml glass standard flasks with distilled water.

Microwave digestion with aqua regia and hydrofluoric acid: Smaller portions of sample (0.25 g) were treated with 6 ml of *aqua regia* and, after 5 minutes, with 4 ml of hydrofluoric acid. They were left to stand at room temperature, with a loosely fitted lid, for 30 minutes, after which the vessels were closed and heated with the same programme as for *aqua regia*. When cool, the vessels were opened, 3.0 g powdered boric acid added to each, closed again, and digested for a further 20 minutes at 50% power. After cooling a second time, the vessels were opened, and the contents filtered through glass fibre papers into 25-ml polyethylene standard flasks and made to the mark with distilled water.

Nitric acid/peroxide digestion: Portions of sample (2.5 g), were weighed into borosilicate glass beakers, treated with 5 ml of concentrated nitric acid added dropwise over 10 minutes to avoid too vigorous a reaction, followed by 2 ml of 30% w/v hydrogen peroxide. After 30 minutes the beakers were placed on a ceramic hotplate, heated slowly to 50–60 °C (as indicated by a thermometer placed in a beaker containing only water) and held at that temperature for 1–2 hours. The beakers were then left to cool and to stand overnight. The next morning, a further 5 ml of acid and 2 ml of hydrogen peroxide were added to each beaker and the solutions were boiled for about an hour. When cool, the solutions were decanted into 100 ml standard flasks, followed by two washings with distilled water, and made to the mark with more distilled water.

EDTA extraction: Portions of sample (1 g) were treated each with 25 ml of 0.01 *M* EDTA, adjusted to pH 7 or to pH 11, in 30-ml Sterilin vials, with slow rotary agitation for two hours. The vials were then centrifuged and the supernatant liquid in each was aspirated directly out of the vial into the atomic absorption spectrometer. Though smaller sample portions were taken for this extraction than for the acid digest, the limits of detection in the sediment were rather similar, as the limits in terms of $\mathrm{mg \cdot l^{-1}}$ of solution (calculated from standard deviations of the blanks) were significantly lower than with the acid extracts.

Quantification of the Heavy Metals

Most metals (Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn) were determined by atomic absorption spectrometry with an air-acetylene flame. Mercury was determined by cold-vapour AAS. A stock solution of around $1000\,\mathrm{mg \cdot l^{-1}}$ was prepared for each metal, either from the metal itself (Cu, Zn) or from the nitrate, except for Cr for which K_2CrO_4 was taken and reduced in acid solution with hydrogen peroxide to give Cr(III). The solutions prepared from the nitrates were checked by EDTA titration, standardised against pure zinc metal, and then the calculated volume of each was diluted to give a working standard of $100.0\,\mathrm{mg \cdot l^{-1}}$. These were in turn used to prepare a set of multi-element standards containing 0.3, 1.0, 2.0, 3.0, 5.0, 7.5 and $10.0\,\mathrm{mg \cdot l^{-1}}$ of each metal, and all in 1% v/v nitric acid. Instrumental conditions are summarised in Table 1.

Mercury was determined by cold-vapour atomic absorption spectrophotometry with background correction, using tin(II) chloride in hydrochloric acid as the reductant.

Results and Discussion

The Methods of Attack

Five methods of sample attack have been investigated. The results have been assessed in terms of their repeatability, which should indicate whether or not we are

Table 1. Instrumental parameters for atomic absorption determinations

Element	Wavelength, nm	Lamp current, mA	Range, $mg \cdot l^{-1}$	Lim. det., $mg \cdot l^{-1}$	Lim. det., $\mu g \cdot g^{-1}$
Cadmium	228.2	5	0.3–5	0.05	1
Chromium	357.9	7	0.3–7.5	0.1	2.5
Copper	324.8	4	0.3–10	0.1	2.5
Iron	248.3	15	1–10	0.15	4
Lead	217.0	8	1–10	0.2	5
Manganese	279.5	7	0.3–10	0.05	1
Mercury	253.6	4	20–100 ng	5 ng	0.25
Nickel	232.0	8	0.3–10	0.2	5
Silver	328.1	4	0.3–7.5	0.1	2.5
Zinc	213.9	6	0.3–3	0.1	2.5

dealing with a robust operationally defined parameter, and in terms of their relation to results obtained by other methods of attack. Because we wish to overcome the problem of kinetic stability (particularly of natural barium sulphate), we have come to prefer hot digestion, in closed vessels, with microwave heating, because this can be much better controlled than can heating in an open beaker on a hotplate, and because for certain elements, it avoids the problems of loss through the formation of volatile compounds. Nevertheless, we have also used cold extraction with gentle end-over-end agitation of the suspended solids for periods of several hours.

EDTA, pH 7

Our procedure is based on the standard procedure for metals in soils [5], which has been the subject of a recent inter-laboratory comparison [8] from which it was concluded that while there were some difficulties with manganese, the agreement between laboratories was otherwise good, but that it would be desirable for participating laboratories to have an internationally certified reference material on which to test their own performance. This reagent has been compared with EDTA, pH 11.

EDTA, pH 11

This extractant was chosen because it was felt that the higher pH should enhance its complexing powers, particularly with regard to the alkaline earth metals, Ca, Sr and Ba, which should in turn bring into solution other metals trapped in the $BaSO_4$ crystal lattice. This has been proposed by Sen Gupta for the determination of rubidium and strontium in barytes [9]. Our tests were aimed at both the Rio Odiel sediments and the North Sea drilling cuttings sediments. Tables 2 and 3 summarise some of the results obtained. The significance of differences in values is judged in terms of the variability of the results at one pH: the range of values for triplicate tests was usually of the order of ±5% to ±10%.

When the individual sets of data were analysed, good correlations could be seen, for the drilling cuttings, between the extractabilities of copper and of nickel at the

Table 2. Mean recoveries of metals by EDTA extraction (% relative to *aqua regia* digest) from acid polluted river sediment (Rio Odiel): extraction at pH 11 vs. pH 7

	Cr	Cu	Mn	Ni	Pb	Zn
Mean extractability at pH 11, %	8	18	72	33	37	45
Mean extractability at pH 7, %	7	25	80	35	34	49
Average R_{11}/R_7 %	115	75	90	94	108	92
Significant?	no	yes	no	no	no	no

Table 3. Mean recoveries of metals by EDTA extraction (% relative to *aqua regia* digest) from North Sea drilling cuttings: extraction at pH 11 vs. pH 7

	Cr	Cu	Mn	Ni	Pb	Zn
Mean extractability at pH 11, %	11	16	73	31	35	47
Mean extractability at pH 7, %	6	19	81	29	31	48
Average R_{11}/R_7 %	177	84	90	107	113	98
Significant?	yes	no	no	no	no	no

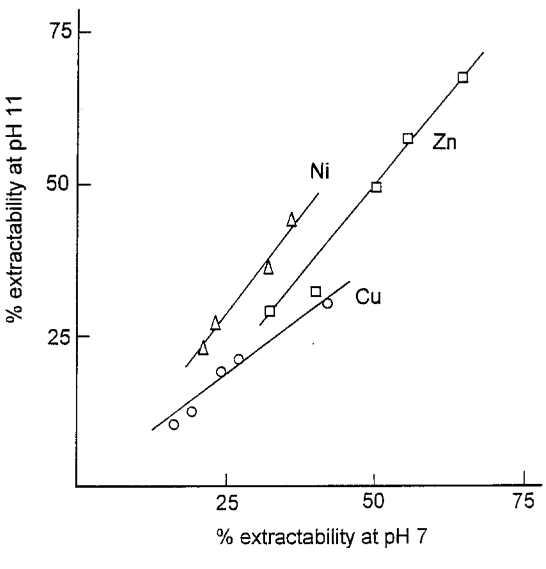

Fig. 1. Correlation of extractability of metals from drilling cuttings by EDTA at pH 11 vs. EDTA at pH 7

two pH's. The data, shown in Fig. 1, do help to reinforce the idea that EDTA extraction is indeed quite a robust method, at least for some metals. The different % extractabilities could be related to different pH's at different depths in the original cuttings pile.

The extractabilities correlated well for Cu, Ni, and Zn in the drilling cuttings except for the very high pH sediment samples (probably with high cement contents), from which more copper, nickel and zinc is extracted at pH 7 than at pH 11, as can be seen fo the correlation data in Table 4. The correlation for lead is not good – if it is present as sulphate, or perhaps bound in the lattice structure of the barite in the

Table 4. Correlation of metal extractabilities from drilling cuttings into EDTA at different pH's

	Copper	Nickel	Lead	Zinc
Slope, pH 11 vs. pH 7	0.71	1.30	0.82	1.23
Correlation coefficient, r^2	0.93	0.98	0.59	0.98

Table 5. EDTA-extractable fractions (pH 7) of heavy metals in the Odiel sediments

	% EDTA-extractable					
Site	km	pH	Cu	Mn	Pb	Zn
Above the mines	4	7.6	<1	58	<1	2
Salt marsh	94	3.2	8	7	4	24
Estuary	111	6.6	31	23	57	44

cuttings, this would not be suprising, as apparent extractability depends very much on sample size and amount of baryte present, and its solubility is easily exceeded.

EDTA Extractabilities for Metals in the Spanish River Sediments

It seems fairly clear that the mechanism for transport of the metals in the Rio Odiel depends on solubilisation by the high acidity (pH 2.5 just below the mines). These metals are then precipitated several tens of kilometers downstream when the pH rises due to mixing with other waters. Table 5 compares the extractabilities of several metals at three different sites in this river.

The low concentrations of metals in the sediments of the clean mountain river above the mining area are in native geological material, unreactive and insoluble, and so are not seen by an EDTA extraction. By the time the metals are being dumped far down the river, as finely dispersed particles, as a consequence of a rise in pH, they are readily extractable.

The conclusion is that for most metals there is little difference in the results for the two pH's, from which we can conclude that the extraction procedure is rather robust, at least for these two very different classes of sediments, in which % extractabilities can vary according to pH of the river or depth in the drilling cuttings core. Indeed, the ratios of the mean extractabilities for these two classes of sediments are remarkably close.

Nitric Acid with Hydrogen Peroxide

This has been recommended, particularly for sulphide-containing sediments, to bring elements such as arsenic into solution, while avoiding its possible loss as the volatile chloride, which might arise in the use of *aqua regia.*

Table 6. Mean recoveries of metals (% relative to *aqua regia* extraction) in drilling cuttings by nitric acid/peroxide digestion vs. *aqua regia* digestion

	Cr	Cu	Mn	Ni	Pb	Zn
Mean level, mg/kg, HCl/HNO_3	51	53	870	52	180	361
Average recovery, % HNO_3/H_2O_2	89	96	94	93	69	98
Significant?	no	no	no	no	yes	no

Aqua Regia

This 3 + 1 v/v mixture of hydrochloric acid with nitric acid is recommended by the Standing Committee of Analysts, 1986, for the extraction of heavy metals in soils and sediments [5].

These two nitric acid digests have been compared for the determination of several metals in the drilling cuttings, and a generally good agreement was found, as can be seen in Table 6. The recovery of lead by nitric acid/peroxide is significantly low compared to that by *aqua regia*, but once again, this is probably due to the lead being present as the sulphate.

Good agreement here does tend to suggest that we are recovering "all" the metals by both methods, or at least, all of the metals which are available to strong acid attack, and possibly all of those which are of "recent" origin.

While the use of closed vessels with microwave heating is becoming more widely adopted for the determination of metals in sediments, sample treatment in open beakers is certainly valid for some metals, though contamination from airborne dust might be more of a hazard for common elements in this case. Quevauviller et al. have compared the acid extraction of many metals from several standard reference materials using open beaker digestion on a hotplate and closed vessel digestion with microwave heating, with rather short heating times of typically 5–10 minutes, and found generally good recoveries [10]. Comparisons for manganese, sometimes considered a difficult element, and for cadmium, obtained in our laboratory, are shown in Fig. 2 and Fig. 3.

On account of the larger scatter of results for cadmium, resulting at least in part from the rather low levels present, no significant difference can be detected between the two sample decomposition techniques, but for manganese, where the correlation is very good, we can see that manganese by open-beaker attack is about 98% of that found by closed vessel attack in the microwave oven.

The Problem of Barium

There is certainly one problem element in the North Sea drilling cuttings-barium. Recoveries of barium in these samples are very low indeed, which is in line with the low solubility product of $BaSO_4$, $K_{sp} = 10^{-10}$. Calculations would suggest that EDTA should dissolve baryte at pH 10, and indeed this has been proposed as a means of quantifying trace elements in the crude mineral [4]. However, we have

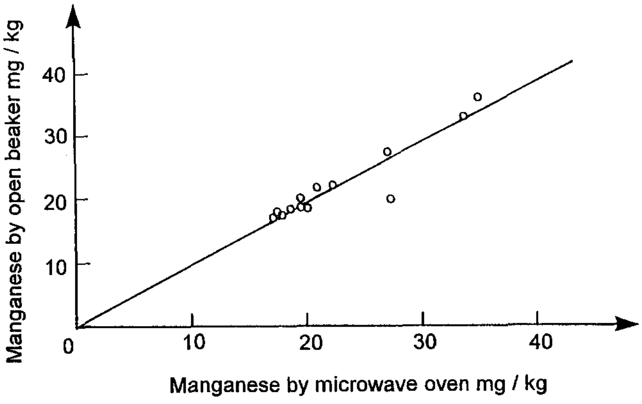

Fig. 2. Correlation of manganese levels in drilling cutttings: digestion in *aqua regia* in an open beaker on a hotplate vs. digestion in a closed vessel with microwave heating

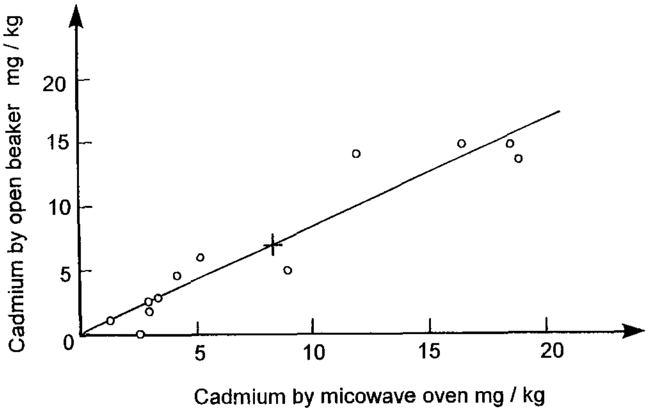

Fig. 3. Correlation of cadmium levels in drilling cuttings: digestion in *aqua regia* in an open beaker on a hotplate vs. digestion in a closed vessel with micowave heating

found that, first, dissolution of natural barytes is very slow, even with heating in the microwave oven, and second, that the solubility is rather limited, so that not more than 50 mg of the material can be safely taken into 20 ml of 0.1 *M* EDTA, even at pH 12. This illustrates the importance of considering sample size and reagent volume when reporting on extractable levels of trace elements. A summary of the recoveries of barium using different attacks is given in Table 7. The samples were taken at different depths in the accumulated cuttings pile on the sea bottom.

It is clear that normal acid attacks are quite useless for extracting barium, and that EDTA at pH 12, while it is somewhat better, is still very far below the efficiency of a fusion. We now prefer to use a sodium carbonate fusion – it is faster to attack

Table 7. Dissolution of barium sulphate: barium in oil-well drilling cuttings

	Sample depth					
Method	30 cm	60 cm	90 cm	120 cm	150 cm	180 cm
$LiBO_2$ fusion %	11.5	8.0	7.7	7.0	10.3	5.6
HNO_3/H_2O_2 mg/kg	8	11	<2	<2	<2	11
EDTA, pH 12 mg/kg	2280	960	5800	11360	7040	9120

and faster to dissolve after cooling, than is the lithium metaborate. This will be the subject of another more detailed report elsewhere.

Aqua Regia with Subsequent Addition of Hydrofluoric Acid

The use of hydrofluoric acid on its own has been recommended for the dissolution of residues insoluble in *aqua regia* [5]. The combination of *aqua regia* with hydrofluoric acid has been proposed with the aim of achieving a "total solubilisation" of all metals in a sample [6]. The samples are contained in sealed PTFE vessels, and heated by microwave power. Loring and Rantala's reasons for adopting this digestion procedure in preference to all others have been summarised in the Introduction. This paper now reports results for these two acid attacks on two widely used CRM's, and on the three sets of samples.

The Performance of the Methods – Repeatability

Certified Reference Materials PACS-1 and MESS-1 were each analysed five times to obtain mean values and standard deviations – results in Tables 8 and 9 respectively.

In most cases the relative standard deviations are quite low, at rarely over 6%, for either acid combination. The absolute values found for the metals are in some cases significantly different from the certified values, but yet give similar values by the two acid digests (Cr and Mn). Presumably significant proportions of these two metals are present in these sediments as silicates which are not attacked by these acid digestions. Copper, nickel and zinc values by both digestion procedures come acceptably close to the certified values for the CRM's. Mercury is a special case in that the agreement for PACS-1 is excellent, but for MESS-1 (where the concentration is much lower) it is very poor: possibly there was a contamination problem in addition to that of measuring very small signals. Cadmium levels were in all cases too small to be measured with confidence. The recoveries are summarised in Table 10.

Table 8. Accuracy and precision of the *aqua regia* digestion procedures – PACS-1. Data based on $n = 5$ digestions

	Certified value	*Aqua regia*		*Aqua regia* + HF	
Element	$mg \cdot kg^{-1}$	$mg \cdot kg^{-1}$	r.s.d., %	$mg \cdot kg^{-1}$	r.s.d., %
Cr	113	56	3	64	4
Cu	452	375	5	344	2
Hg	4.6	4.6	6	4.5	4
Mn	470	275	4	340	4
Ni	44	39	3	48	6
Pb	404	350	5	346	7
Zn	824	735	3	755	5

Table 9. Accuracy and precision of the *aqua regia* digestion procedures – MESS-1. Data based on $n = 5$ digestions

Element	Certified value	*Aqua regia*		*Aqua regia* + HF	
	$mg \cdot kg^{-1}$	$mg \cdot kg^{-1}$	r.s.d., %	$mg \cdot kg^{-1}$	r.s.d., %
Cr	71	26	3	40	15
Cu	25	20	1	24	6
Hg	0.17	0.25	6	0.48	10
Mn	513	305	5	382	5
Ni	30	25	3	35	4
Pb	34	22	10	51	4
Zn	191	172	1.5	184	8

Table 10. Recoveries of metals in CRM's relative to certified values %

Element	*Aqua regia* MESS-1	PACS-1	*Aqua regia* + HF MESS-1	PACS-1
Cr	37	49	56	57
Cu	80	83	97	76
Hg	147	101	275	98
Mn	60	58	75	73
Ni	84	87	118	108
Pb	65	87	150	86
Zn	90	89	96	92

Analysis of the Sediment Samples

It is proposed now to make some comparison of the results obtained for the metals in the three classes of sediments, using the two strong acid attacks.

The site O2 represents a clean stretch of the river above the mining area, with low levels of metals in the sediments. The EDTA extractabilities of the metals in these sediments are very low, which would suggest that the metals are present in native geological minerals. While the HF method gives higher values for Ni and Pb, it also gives lower values for Cu and Zn.

The site O8 represents a heavily contaminated site where the metals have been precipitated out of solution by a rise in pH brought about by the mixing of two river streams. The metals here are readily extracted by EDTA. The differences in the results by the two *aqua regia* digests are not really significant here either, except perhaps for zinc.

The Clyde estuary sample was digested in triplicate by each of the methods, and the metals determined as before by atomic absorption spectrometry. The results are summarised in Table 12.

Table 11. The Rio Odiel neutral sediments, concentrations of metals, mg·kg^{-1}

Element	Clean sediment of fresh mountain water pH 6.6 – [O2]		Polluted sediment, in saline water pH 7.4 – [O8]	
	Aqua regia	*Aqua regia*+HF	*Aqua regia*	*Aqua regia*+HF
Cr	n.d.	n.d.	36	22
Cu	20	12	270	300
Hg	0.6	0.5	18	11
Mn	427	307	392	347
Ni	13	22	40	36
Pb	26	38	640	740
Zn	79	56	650	435

n.d. = not detectable.

Table 12. The Clyde sediment No. 1 (surface), concentrations of metals, mg·kg^{-1} ± s, $n = 5$ digests

Element	Aqua regia	Aqua regia + HF
Cr	135 ± 20	129 ± 15
Cu	100 ± 10	101 ± 12
Hg	0.7 ± 0.1	1.1 ± 0.2
Mn	231 ± 20	236 ± 23
Ni	31 ± 4	23 ± 5
Pb	132 ± 15	153 ± 25
Zn	250 ± 30	235 ± 23

Table 13. North Sea drilling cuttings sediment (90 cm), concentrations of metals, mg·kg^{-1} ± s, $n = 3$ digests

Element	EDTA, pH 7	*Aqua regia*	*Aqua regia*+HF
Cr	n.d.	35 ± 1	46 ± 3
Cu	8	43 ± 2	56 ± 7
Hg	<0.2	0.7 ± 0.1	1.2 ± 0.2
Mn	210	917 ± 65	855 ± 38
Ni	6	54 ± 2.5	43 ± 2.4
Pb	66	250 ± 9	253 ± 15
Zn	—	993 ± 85	646 ± 51

We can conclude that there are no significant differences for the trace metals in the surface sediment of the Clyde estuary as found by the two digests. Use of the HF method therefore offers no advantage for these samples.

The North Sea drilling cuttings sediment was cored and a sample from 90 cm depth was analysed by three procedures including with EDTA extraction, each in triplicate. These results are summarised in Table 13.

The metals in the drilling cuttings are moderately extractable with EDTA (cold extraction at pH 7) but there is no pattern of higher levels being found for the HF digest. Indeed, the differences are once again hardly significant, except for zinc, where the HF result is significantly low. We should note here that neither acid digest makes much impression on the natural barytes, so heavy metals such as lead and mercury in the barytes are likely *not* to be seen by these acid digests. As discussed earlier, a fusion method seems to be the only route to a reasonably complete analysis for "total" metals in these sediments.

Conclusions

The comparison of analytical results for the three very different sets of contaminated sediments seems to point clearly to the conclusion that there is no need for an HF attack when heavy metals are to be determined. Subtle differences in the concentrations in varying mixtures of "native" or "geological" material as distinct from recently deposited anthropogenic material, are likely to be masked by the larger variation in the extraction processes themselves. On some samples the agreement between replicates is excellent, while in the next it can be very poor, with no obvious explanation. The comparison of EDTA-extractabilities with *aqua regia*-extractabilities would seem to offer a satisfactory route for distinguishing these different forms of the metals.

What remains to be shown, of course, is to what extent the metals are also bio-available, to living organisms in the estuary – mussels, shrimps and so on. Recent work in our laboratories has shown that mussels, *Mytilus edulis*, can accumulate especially lead and zinc from the North Sea drilling cuttings, in which an appreciable fraction of the metals are EDTA-extractable, and in which high concentrations are acid-extractable. We hope, in due course, to be able to gather enough data to enable correlations to be attempted between chemical extractabilities and uptake rates by mussels and small shrimps. This work is in progress at present.

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