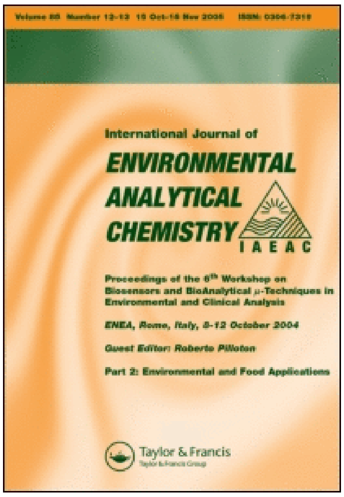

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NEW SEDIMENT AND SOIL CRMs FOR EXTRACTABLE TRACE METAL CONTENT

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The lack of uniformity in leaching procedures used to measure broadly defined forms of heavy metals does not allow the results to be compared world-wide nor the methods to be validated since the results obtained are "operationally defined". An attempt was made to certify several mineral soils CRMs for single extraction by using acetic acid, EDTA and DTPA for Cd, Cr, Cu, Ni, Pb and Zn. Recently, to complete the series of soil CRMs, an organically enriched soil was prepared SO25. For sediments a CRM 601 was produced and certified for metals extractable by using the BCR three step sequential extraction. Not all the trace elements were certified and only indicative values were given for some of them due to poor reproducibility. We performed a systematic study of the effect of the variables identified as potential sources of uncertainty in the use of this scheme. With this study the sources of uncertainty were revealed and an optimised version of the protocol was proposed. With this new version it was possible to certify all the trace elements studied. New sediment material S33 is now proposed for certification and additional data are given for the sediment CRM 601. This modified procedure was also applied to a soil CRM 483 and good results were obtained. This procedure may thus be applied to polluted soils.

Keywords: Single extraction; sequential extraction; CRM; heavy metals; soils; sediments

INTRODUCTION

The mobilisation of heavy metals from soils or sediments is governed by three main factors, the characteristics of the solid phase, the chemistry of the element and the environmental conditions. Depending on their origin, heavy metals occur in soils and sediments in different forms. In the environment heavy metals in soils and sediments are continuously establishing equilibrium between the solid phase and the soil solution or pore water. At any time the fraction of metal which is in equilibrium with the liquid phase comes from the less retained fractions in

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the solid and with time some fractions of heavy metals which initially were not mobile become available for the liquid-solid equilibrium. This process is more significant when environmental conditions change. In addition the solid-liquid equilibrium may be displaced leading to the introduction of a significant amount of pollutant into the liquid phase, and so increasing mobilisation.

In environmental studies at laboratory level, extraction procedures are used to ascertain the potential mobilisation of heavy metal from a soil or sediment[1]. For this purpose two strategies are considered. The first is the prediction of short-term heavy metal mobilisation, which is based on the determination of the labile heavy metal fraction. The second one *i.e.* the prediction of long term heavy metal mobilisation, is based on the determination of the available fraction. This fraction is not constant with time and may increase when environmental conditions change entailing variations in the distribution of heavy metal in the different phases of soils or sediments. The labile and available fractions are measured in various laboratories by batch or continuous leaching, but experimental conditions differ. In batch systems single extraction schemes are applied to soils and sequential extraction to sediments. As extraction procedures attempt to model complex environmental processes, the results obtained are operationally dependent and thus not strictly comparable.

The extractant solutions used in single extraction schemes in soils may be classified in four groups: unbuffered salt solutions, buffered salt solutions, chelating agents and acids.[1] Unbuffered salt solutions are used at concentrations ranging from 10^{-2} mol/L to 1 mol/L. Low concentrations simulate the rain or the composition of the soil solution, and higher concentrations are used to obtain data on the exchangeable fraction. These types of extractions are considered as standard methods in Germany (NH_4NO_3 1 mol/L), The Netherlands ($CaCl_2$ 0.1 mol/L) and Switzerland ($NaNO_3$ 0.1 mol/L) for the evaluation of heavy metal mobility in polluted soils. Buffered salt solutions, mainly ammonium acetate/acetic acid, are used at 1 mol/L at pH 4.8 and pH 7, and give information on the exchangeable fraction at a given pH, which is not the intrinsic pH of the soil. Chelating agents, mainly EDTA for mineral soils and DTPA for calcareous soils are used at various pH values. EDTA has been adopted as a standard method in several countries such as France and United Kingdom, at pH 7, and Italy, at pH 4.6. Chelating agents are used in an attempt to reproduce the mobility of heavy metals, mainly Cu, Zn, Fe and Mn in agricultural soils. Finally acid extraction is used in a wide range of conditions, from weak diluted acids such 0.1 mol/L acetic acid, used to simulate the effect of environmental acidification, to concentrated strong acids such *aqua regia*, used to determine pseudo-total content (total except the fraction bound to silicates).

Sequential extraction schemes are mainly applied to sediments and were initially designed for determining specific chemical species or binding forms[2]. These schemes are widely applied, but it is now accepted that they are not as selective as desired and that the information obtained with them cannot be directly related to binding forms in the solid phase. More recently sequential extraction was applied for the determination of more broadly defined forms: exchangeable, acid leachable, oxidisable or reducible, depending on operationally defined procedures[3]. The information obtained from sequential extraction schemes can help to predict the risk of environmental contamination. So these procedures are increasingly being applied to sediments and, recently, even to soil samples after an accidental spillage[4]. By applying sequential extraction to soils affected by the Aznalcollar accident[5], it was shown that major elements were mainly, but not selectively, associated to fractions considered in early stages as related to specific phases, *i.e.* Ca and Mg were mainly associated to the fraction solubilised with acetic acid (70–90%) commonly called carbonated fraction or aluminium was associated to the residual fraction (90–95%).

As the results obtained by applying leaching procedures is procedure dependent, there is no fully satisfactory method available, and attempts are being made to improve existing methods or adapt them to specific problems or circumstances. As a result a large number of procedures have emerged, using not only different types of extractant solutions, including different pH values for the same extractant, but also a variety of laboratory conditions[6]. The main variables which are modified may be summarised as follows: solid/Liquid ratio, time of extraction, temperature, shaking intensity and type of shaking, the method for liquid-solid separation, the use or not of inert atmosphere. As all these factors affect the results obtained leaching procedures in general cannot be compared directly.

THE EUROPEAN APPROACH

In 1987 the Community Bureau of Reference launched a programme aimed at harmonising extraction procedures, single and sequential, for the determination of trace metals in soils and sediments. The program started with a literature survey and a consultation with European experts[3]. They identified the main requirements for procedures that could be widely accepted and able to be used with legislative purposes. These needs were summarised as single extraction for soil and sequential extraction for sediments. The pollutants considered to have priority were Cd, Cr, Cu, Ni, Pb and Zn and the need to prepare certified reference materials (CRM's) for their extractable trace metal content to be used in method validation in control laboratories was pointed out. As a complement to this study, some interlaboratory exercises with the participation of expert laboratories took place from 1987 to 1990 and the outcome of the survey and the results of the interlaboratory trials were discussed in a workshop in 1992. The interlaboratory exercises showed the need for a better definition of the protocols used in order to obtain results that would be reproducible among laboratories.

In the workshop[7] the participants agreed on the need to move together in the direction of harmonising the extraction protocols among European countries. As a starting point well described single extraction protocols for soil, based on acetic acid and EDTA, and for sediment, based on a three-step sequential extraction protocol, were adopted. Moreover the need to prepare reference materials for extractable contents based on these procedures was again pointed out.

In the third Framework programme of the European Commission a project was developed (ETMESS) for validating the extraction procedures and for the preparation of CRMs. As a result of this project, the first CRMs for the extractable content of trace metals from soils and sediments were prepared. Four CRMs, three soils and one sediment, prepared within this project are now available through the Institute for Reference Materials and Measurements. The three soil reference materials are CRM 483 and CRM 484, two sewage sludge-amended loamy soils with low organic matter content, and CRM 600, a calcareous soil and the sediment reference material is CRM 601. The materials studied are given in Table I.

TABLE I Reference materials certified or ready for certification for extractable trace metal using single and sequential extraction procedures

Reference material	*Procedures applied*
CRM 483 sewage sludge amended soil	Acetic acid, EDTA and *aqua regia* Improved version sequential extraction procedure
CRM 484 sewage sludge amended soil	Acetic acid, EDTA and *aqua regia*
CRM 600 calcareous soil	EDTA and DTPA
SO25 organic matter enriched mineral soil	Acetic acid and EDTA
CRM 601 sediment	Sequential extraction procedure (original and improved version)
S33 sediment	Improved version of sequential extraction procedure.

All three soils are certified for their extractable contents of Cd, Cr, Cu, Ni, Pb and Zn. CRM 483 and CRM 484 are certified for the extractable amounts obtained by using 0.43 mol/L acetic acid and 0.05 mol/L EDTA and CRM 600 by using 0.1 mol/L DTPA and 0.1 mol/L EDTA. The extractable contents are shown in Table II. The values in italics and brackets are indicative only and were not certified due to a suspicion of instability.

TABLE II Certified values and uncertainties (expressed in mg/kg) for EDTA, DTPA and acetic acid-extractable contents in BCR certified soils reference materials

Material	*Extractant*	*Cd*	*Cr*	*Cu*	*Ni*	*Pb*	*Zn*
CRM 483	Acetic acid	18.3	18.7	33.5	25.8	2.10	620
		(0.6)	(1.0)	(1.6)	(1.0)	(0.25)	(24)
CRM 483	EDTA	24.3	28.6	215	28.7	229	619
		(1.3)	(2.6)	(11)	(1.7)	(8)	(19)
CRM 484	Acetic acid	0.48	n.d.	33.9	1.69	1.17	193
		(0.04)		(1.4)	(0.15)	(0.16)	(7)
CRM 484	EDTA	0.51	n.d.	88	1.39	47.9	152
		(0.03)		(4)	(0.11)	(2.6)	(7)
CRM 600	DTPA	1.34	(0.014)	(32.3)	3.31	(15.0)	(142)
		(0.04)			(0.13)		
CRM 600	EDTA	2.68	0.206	(57.3)	4.52	59.7	383
		(0.09)	(0.021)		(0.25)	(1.8)	
SO 25	Acetic acid	67.5	19.0	36.3	99.0	4.85	719
		(2.8)	(1.1)	(1.6)	()5.1	(0.38)	(24)
SO 25	EDTA	65.2	10.1	89.4	53.2	103	510
		(3.5)	(0.9)	(2.8)	(2.8)	(5)	(7)

The requirements of a CRM, i.e., homogeneity, stability, similarity to a real sample, accuracy, known uncertainty and traceability, were accomplished for mineral and calcareous soils. The homogeneity was accomplished for samples at 5 g intake. Stability of the material for its extractable contents was shown for all of the materials. The accuracy was accomplished by following a very well described protocol and certifying extractable contents via a certification exercise among expert laboratories and traceability of the results was achieved by using traceable calibrants. The results obtained are procedure-specific[8,9].

For sediments the CRM 601 was produced and certified for its extractable contents of Cd, Cr, Cu, Ni, Pb and Zn by applying the three-step sequential extraction scheme[10]. The amounts certified are given in Table IV. Two round robin exercises were carried out before the certification round to check the scheme. The results showed the need for improvement before attempting the certification of a reference material for three consecutive steps and for six elements. In the protocol the sample is first treated with acetic acid to liberate exchangeable/acid-extractable metals, and the metals associated with the reducible phase are then solubilised by using hydroxylamine hydrochloride (second step). Finally, the metals are released by hydrogen peroxide (step 3).

Although a more detailed protocol was applied in the intercomparison exercise, the spread of the results was still too great, showing poor reproducibility in the second and third steps. This spread of results could not be attributed to heterogeneity, as the homogeneity of the material was checked and accomplished for 1 g sample intake. The stability of the material for extractable contents was tested to determine the suitability of the sediment as reference material. Sets of bottles were kept at –20, +20 and +40°C for twelve months. Extractable contents were determined periodically. As instability indicator the ratio between the extractability of samples stored at different temperatures with those stored at –20°C was given. In the case of ideal stability the ratio should be 1. Some instability were found for extractable Cu in samples stored at 40°C probably due to changes in the status of the organic matter or in the crystallographic compounds of Fe and Mn. The spread of results was accepted by the expert laboratories to be the state of the art for this type of measurement in this type of material.

THE NEW CRM FOR EXTRACTABLE TRACE METAL CONTENT

The success in the application of validated procedures for soils and sediments and the widespread use of the CRM already prepared for extractable contents highlighted the need to develop additional CRMs. Organic soils were considered to be as the most appropriate for certification of extractable heavy metal content in single extraction methods. A new CRM for sediment would need to be prepared for sequential chemical extraction after refining the procedure. It was also decided to assess whether the sequential extraction scheme could be applied to soil samples.

In the 4th Framework programme of the European Commission a new project was presented and approved for preparing new CRMs for their extractable trace metal content in soils and sediments. The new materials proposed were a soil enriched in organic matter, SO25, for certifying extractable heavy metal content by using acetic acid and EDTA, and a sediment, S33, for the application of an improved three-step sequential chemical extraction. Moreover prior to certification it was proposed to carry out a study to overcome the sources of error in applying the three-step sequential extraction to sediment and to apply it as a feasibility study to a soil material. For this purpose it was chosen the already certified sediment material CRM 601 and the sewage sludge amended soil certified for its extractable contents by applying single extraction, CRM 483. In this context two new materials were prepared: SO25, a soil enriched in organic matter, and S33, a new sediment sample. In addition, after applying the modified procedure to the soil and the sediment samples, new information has become available for CRM 483 and CRM 601 (Table I).

SINGLE EXTRACTION PROCEDURES: SO25

To complete the series of reference materials certified for their extractable contents using acetic acid and EDTA, a new mineral soil, SO25, enriched in organic matter has been produced in order to provide users with a different soil-matrix type. This material is suitable for certification. Homogeneity has been checked as for the previous CRM for a 5 g sample intake. Stability has been tested in samples kept either at room temperature and at 40°C. The prepared material has been shown to be stable when kept at room temperature for one year, but some changes have been observed in the extractable Cu content induced by high storage temperature. This could be related to changes in the status of the organic matter or in the crystallographic compounds of Fe or Mn. Hence, it is recommended to store the material at +4°C in the dark.

The contents extractable by acetic acid (0.43 mol/L) and EDTA (0.05 mol/L) have been established by applying the same protocols as those used for certifying CRM 483 and CRM 484. As complementary information the aqua regia extractable content of heavy metals in the soil sample has been determined by using the ISO 11466 procedure[11]. All the values have been established through intercomparison exercises among expert laboratories. The results obtained are given in Table II.

SEQUENTIAL EXTRACTION PROCEDURE: IMPROVED VERSION, NEW DATA AND NEW MATERIAL

When materials are prepared for certification of total metal content it is generally straightforward to specify recommended values and their associated uncertainties. Special difficulties exist, however, when the species to be determined are isolated *via* an operationally defined procedure. Small operational variations can lead to non-comparability. These difficulties are magnified when several operationally defined steps are used sequentially as occurs when applying the sequential extraction procedure. In the CRM 601 five elements, Cd, Cr, Ni, Pb and Zn, could be certified in the first step. Cu was not certified due to some doubts on the stability of the material in relation to the extractable Cu content. In the second and third steps only three elements could be certified due to the high variability between results obtained by different laboratories.

To overcome the lack of reproducibility a systematic study of variables identified as potential sources of uncertainty in the use of the three-step sequential extraction was carried out. The effects studied in the second step were: extractant pH within the range pH 1.0–3.0 (10 different pH values), extraction temperature (20°C, 26°C and 40°C), extraction time (from 2 to 24 hours) and extractant concentration (0.1, 0.5 and 1mol/L) together with the effect of the type of acid used in pH adjustment (HNO_3 or HCl), the effect of an inert atmosphere (nitrogen), and the method used to separate liquid and solid phases (centrifugation and centrifugation plus filtration). The use of alternative reagents, such as ammonium hydrogen oxalate and oxalic acid, was also considered. The study focused on the second step since previous work had indicated that this was the major source of uncertainty. Experimental details and the obtained results are given elsewhere.[12]

TABLE III Systematic study on the effect of variables identified as potential sources of uncertainty

Variable	*Range or alternative*	*Effect*
The pH of the extractant	1.0 – 3.0	Paramount importance
Type of acid	HNO_3 or HCl	None
Temperature	20°C – 40°C	None
Time	2 – 24 hours	Yes, up to 8 hours then none
Inert atmosphere	air or nitrogen	None in air dried samples
Method used for separate liquid and solid phases and centrifugation conditions	centrifugation or centrifugation + filtration	None
	1500 to 5000g	Yes up to 5000g
Increasing extractant concentration	0.1 to 1.0 mol/L	Yes, up to 0.5
Alternative reagents	ammonium hydrogen oxalate oxalic acid	No recommendation

TABLE IV Results obtained in the interlaboratory study on long-term stability (24 months) of the extractable metal contents in the sediment reference material CRM 601 using the original extraction procedure

	Certified value (mg kg^{-1})	*Uncertainty (mg kg^{-1})*	*Long-term stability value (mg kg^{-1})*	*Uncertainty (mg kg^{-1})*
First step				
Cd	4.14	0.23	4.46	0.63
Cr	0.36	0.04	0.37	0.087
Cu	8.32(*)	0.46	10.4	0.43
Ni	8.01	0.73	8.22	0.83
Pb	2.68	0.35	2.07	0.49
Zn	264	5.0	259	13
Second step				
Cd	3.08	0.17	3.05	0.96
Cr	1.43(a)	1.0	1.42	0.83
Cu	5.69(a)	3.2	6.37	3.56
Ni	6.05	1.1	5.55	1.5
Pb	33.1	10	37.3	19
Zn	182	11	175	15
Third step				
Cd	1.83	0.20	1.80	0.17
Cr	18.3(a)	4.47	19.4	0.91
Cu	116(a)	26	116	9.0
Ni	8.55	1.04	6.75	0.86
Pb	109	13	108	19
Zn	137(a)	30	124	17

a. not certified values obtained in the intercertification campaign.

From this systematic study it was concluded that the pH of the extractant is of paramount importance. An incorrect pH adjustment, as might be obtained with an improperly calibrated pH-meter, could be a major source of irreproducibility. An alternative method of pH adjustment by the addition of a fixed amount of dilute nitric acid was proposed. The type of acid used for pH adjustment, the temperature and working under nitrogen did not strongly influence the precision of the results obtained in step 2 nor did the incorporation of additional filtration after centrifugation for solid-liquid phase separation. The duration of extraction influenced the results, since the amount extracted increased up to 8 hours of shaking then remained constant. As the initial protocol recommended 16 hours no modification was proposed. An improvement in the precision was obtained by increasing the centrifugation force from 1500 to 5000 g and by increasing the extractant concentration to 0.5 mol/L. So an increase in the centrifugation up to 3000 g, available to many laboratories, and in the extractant concentration to 0.5 mol/L was recommended[13]. In Table III the variables studied, the range or the alternative and the magnitude of the effect are summarised.

Once a modified protocol was proposed, an intercomparison study was designed using the existing sediment CRM 601. Seven experienced laboratories participated in the intercomparison exercise. Each was requested to apply both the original sequential extraction scheme and the modified protocol in order to check not only the increase of reproducibility but also to verify the stability of the material in respect of extractable contents. The participants were also invited to determine the aqua regia leachable metals from the original material and from the residual fraction from the third step in order to check the recovery.

The results of the long term stability study confirm the stability of extractable contents of Cd, Cr, Ni, Pb and Zn in this type of material and demonstrate that the preparation of this kind of CRM can be achieved. The values obtained are given in Table IV.

The results confirm the stability of the extractable contents of Cd, Cr, Ni, Pb and Zn in this type of material and the lack of long term stability for Cu. This element had not been certified because of the suspicion of long-term instability inferred from the stability data at 40°C. The results also demonstrate that the preparation of CRMs for extractable trace metal contents in sediments or similar matrices can be achieved.

NEW DATA FOR CRM 601

The second aim of the intercomparison was to apply the modified sequential extraction procedure to the sediment CRM 601 in order to check the increase of precision and to supply to the user additional data on heavy metal extractable contents. Mean values and uncertainties are given for the three steps and for six elements in Table V. Results are expressed as mass fractions of the respective extracts obtained at the first, second and third steps (based on dry mass) in $mg.kg^{-1}$.

TABLE V Mean values and uncertainties obtained with the modified sequential extraction procedure

CRM 601	*Obtained value (mg kg^{-1})*	*Uncertainty (mg kg^{-1})*	*CV (%)*
First step			
Cd	4.45	0.63	14
Cr	0.35	0.08	23
Cu	10.5	0.8	7.6
Ni	7.82	0.84	11
Pb	2.28	1.17	51
Zn	261	13	5.0
Second step			
Cd	3.95	0.53	13
Cr	10.6	0.9	8.5
Cu	72.8	4.9	6.7
Ni	10.6	1.3	12
Pb	205	11	5.4
Zn	266	17	6.4
Third step			
Cd	1.91	1.43	75
Cr	14.4	2.6	18
Cu	78.6	8.9	11
Ni	6.04	1.25	21
Pb	19.7	5.8	29
Zn	106	11	10

The coefficient of variation obtained in the same group of laboratories for CRM 601 by applying the original sequential extraction scheme and the modified one by the same group of laboratories are given in Table VI. The new procedure significantly decreased the dispersion in the second step, mainly for Cr, Ni and Pb. This decrease in the coefficient of variation was achieved in two ways: by applying a better protocol which uses the optimum conditions to achieve reproducibility and by increasing the amount of metal extracted in the second step. This increase is due to a decrease in the pH in the second step, from pH 2 in the original protocol to pH 1.5 and to an increase of the extractant concentration from 0.1 to 0.5 mol/L in the modified procedure. The precision values obtained for this material with the modified protocol is clearly better than those obtained with the original procedure. The poor precision for Cd in the third step with both protocols is due to the fact that the concentration in the extract is too close to the detection limit.

TABLE VI Summary of the results of the interlaboratory study on extractable content Interlaboratory CVs (%) in CRM 601

Steps	*Cd*	*Cr*	*Cu*	*Ni*	*Pb*	*Zn*
Original BCR-Sequential Extraction Protocol						
First	14.2	25.4	7.7	10.1	23.7	4.9
Second	28.6	55.7	65.3	25.6	47.3	8.3
Third	60.9	10.2	7.8	12.2	16.9	13.5
Modified BCR-Sequential Extraction Protocol						
First	15.0	21.9	7.6	10.8	51.3	4.9
Second	13.4	8.3	6.8	12.1	5.5	6.2
Third	74.9	18.1	11.3	20.7	29.6	10.2

The new protocol uses the same extractant solution in the first step but not in the second. In this protocol, the pH of the extractant is lower and the concentration of the reagent is higher than in the original. In consequence, the distribution of the extractable contents of heavy metals between the second and the third step, which are operationally defined changes. The extractability increase is most relevant for Cr, Cu and Pb, which are more sensitive to pH changes. Nevertheless very similar information can be obtained, as not well-defined chemical species are being measured but only broader forms related to mobility caused by reducible or oxidisable conditions. By applying the new protocol, the uncertainty associated to the procedure decreases and consequently the results obtained in different laboratories by applying this improved version should be comparable.

Moreover the accuracy of the results was checked by determining the aqua regia contents (ISO 11466) in the original sample and in the residue of the third step in both procedures (original and modified). The comparison between the sum of the three fractions plus the residue and the aqua regia extractable content show no differences in any case, confirming the good performance of the laboratories participating in the intercomparison. The application of such a procedure to the residue after sequential extraction was considered useful as an internal check on the sequential extraction. The results obtained in an interlaboratory study for aqua regia extractable content are reported elsewhere.[3]

NEW SEDIMENT MATERIAL S33

Once the lack of reproducibility among laboratories was overcome and reproducible results were obtained for the sediment CRM 601, the new challenge was to ensure that the new procedure was good enough to give reproducible results when applied to another sediment sample. With this aim a new sample, S33, was prepared. The sample was shown to be homogeneous at 1 g intake, and stable. A certification exercise was designed among 16 expert laboratories. All of them used traceable calibrants and followed the procedure strictly. The mean values from this exercise together with the coefficient of variation will be published elsewhere. The coefficient of variation obtained in all the values proposed for certification are much better than those obtained when applying the modified sequential extraction procedure to CRM 601, showing the suitability of the proposed method and the good performance of the laboratories. From this intercomparison some recommendations were added to the protocol to ensure proper use of the BCR sequential extraction procedure.

During the certification exercise some laboratories, between 9 and 14 according to the elements, carried out determination of aqua regia extractable content in both the sample and the residue after extraction. Good agreement was found between the sum of the amount extracted in the three steps and the residue and the values obtained by direct extraction of the original material with aqua regia. This material is not going to be certified for aqua regia extractable content but its use can be a useful tool for control purposes when applying the three-step sequential extraction procedure.

NEW DATA FOR CRM 483

Considering the interest shown by soil scientists with respect to the three-step sequential extraction scheme (originally developed for sediment analysis), a trial has been organised to test the suitability of the modified BCR sequential extraction procedure on a soil CRM, namely CRM 483.

As mentioned before this sewage sludge amended soil reference material, CRM 483, was certified for its EDTA and acetic acid extractable contents of some trace elements, following standardised procedures. Before applying the modified three step sequential extraction, the long-term stability of the material was tested. The results show long term stability for EDTA and acetic acid extractable contents of Cd, Cr, Cu, Ni, Pb and Zn. The aqua regia extractable contents following the ISO 11466 norm were also determined. This material contains more Zn and Pb and much more Cr than the sediment S33. Finally the modified BCR sequential extraction procedure was applied to the sample. The results are given in Table VII and show good reproducibility for the three fractions. As before, good agreement was found between the sum of the amount extracted in the three fractions and the residue and the amount directly extracted by aqua regia.

TABLE VII Indicative values: extractable trace metal contents (mg.kg^{-1}) following the BCR-three step sequential extraction scheme in CRM 483

Element	*Mean*	*Standard Deviation*	*CV (%)*
First step			
Cd	10.0	0.77	2.8
Cr	9.4	3.5	37
Cu	16.8	1.5	8.9
Ni	17.9	2.0	11
Pb	0.756	0.70	93
Zn	441	39	8.9
Second step			
Cd	24.8	2.3	9.2
Cr	654	108	17
Cu	141	20	15
Ni	24.4	3.3	13
Pb	379	21	5.5
Zn	438	56	13
Third step			
Cd	1.22	0.48	39
Cr	2215	494	22
Cu	132	29	22
Ni	5.9	1.4	24
Pb	66.5	22	34
Zn	37.1	9.9	27

CONCLUSIONS

CRMs for their extractable content of Cd, Cr, Cu, Ni, Pb and Zn are available for a large set of soil and sediment samples for two single extractants and for a modified three step sequential extraction scheme.

Three single extraction procedures, acetic acid (0.43 mol/L), EDTA (0.05 mol/L) and DTPA (0.1 mol/L), can now be validated in every laboratory by using a defined protocol and the appropriate CRM. By using validated methods, traceable standards and a quality control plan, the results obtained in different laboratories must be comparable.

Homogeneity and stability of soils and sediment samples for their extractable content have been demonstrated, so that the preparation of CRMs for extractable trace metal contents in sediments or soils matrices can be achieved.

The modified BCR three-step sequential extraction protocol improves precision with respect to the original procedure in the second step.

The preparation of a new sediment material S33, the new data for the sediment CRM 601 for the modified three step-sequential extraction and the application of this scheme to soil open new possibilities in environmental studies on heavy metal mobility in soils and sediments.

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References

[1] G. Rauret, *Talanta*, **46**, 449–455 (1998).

[2] A. Tessier, P.G.C. Campbell and M. Bisson, *Anal. Chem.*, **51**, 844 (1979).

[3] A. Ure, Ph. Quevauviller, H. Muntau and B. Griepink, EUR report EN 14472 (European Commission, Brussels, 1992).

[4] M. Vidal, J-F. López-Sánchez, J. Satre, G. Jimenez, T. Dagnac, R. Rubio and G. Rauret, *Sci. Total Environ.*, **242**, 131–148 (1999).

[5] M. Pueyo, J. Sastre, J. F. López-Sánchez and G. Rauret, submitted for publication to *J. Environ. Quality*(2000).

[6] H.A. van der Sloot, L. Heasman and Ph. Quevauviller, eds., *Harmonization of leaching/extraction tests*. Chap. 4, p. 64. (Elsevier, Amsterdam, 1997).

[7] A. M. Ure, Ph Quevauviller, H. Muntau and B. Griepink, *Int. J. Environ. Anal. Chem.*, **51**, 135–151 (1993).

[8] Ph. Quevauviller, G. Rauret, R. Rubio, J.F. López-Sánchez, A. M. Ure, J. Bacon and H. Muntau, *Fresenius J. Anal. Chem.*, **357**, 611–618 (1997).

[9] Ph Quevauviller, M. Lachica, E. Barahona, G. Rauret, A.M. Ure, A. Gómez and H. Muntau, *Fresenius J. Anal. Chem.*, **360**, 505–511 (1998).

[10] Ph. Quevauviller, G. Rauret, J.F. López Sánchez, R. Rubio, A.M. Ure, and H. Muntau, *Sci. Tot. Environ.*, **205** 223–234 (1997).

[11] ISO 11466. Soil Quality. Extraction of trace elements soluble in aqua regia.

[12] A. Sahuquillo, J. F. López- Sánchez, R. Rubio, G. Rauret. R. P. Thomas, C. M. Davidson and A. M. Ure, *Anal. Chim. Acta*, **382**, 317–327 (1999).

[13] G. Rauret, J.F. López-Sánchez, A. Sahuquillo, R. Rubio, C. Davidson, A.M. Ure and Ph. Quevauviller. *J. Environ. Monit*, **1**, 57–61 (1999).