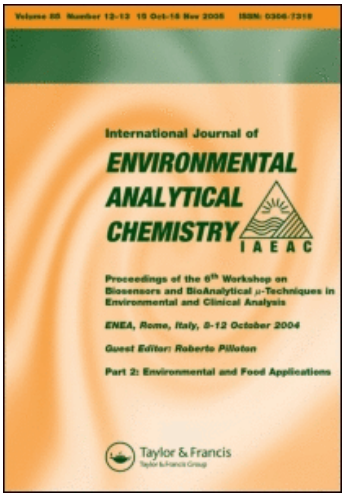

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Kinetic speciation of BCR reference materials

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The accurate study of heavy metal speciation is important in environmental monitoring. There has been much work developing various operationally defined speciation methods for soil and sediment, but there is a need to compare the different approaches by evaluating them for the same sample. In this article, a kinetic method was applied for the heavy metal speciation of the two BCR reference materials, CRM601 and BCR701, which have been specifically developed as materials to evaluate the validated BCR three-step sequential extraction method. When EDTA was used as an extractant, 81.0% of Cd, 68.0% of Cu, 21.5% of Ni, 80.3% of Pb and 71.9% of Zn was extracted from CRM601. For BCR701, the removal ratios were 92.0, 52.3, 18.7, 50.6 and 67.5% with EDTA and 95.7, 25.2, 20.0, 52.4 and 68.5% with hydroxylamine hydrochloride as an extractant, for Cd, Cu, Ni, Pb and Zn respectively. A two-component kinetic model was applied to the extraction curve and the extractable metals were readily classified into two categories, namely, labile fraction and non-labile fractions. The rate constants obtained from the regression model were found to be useful in quantifying the lability of an element. The rate constants obtained from the labile fractions in BCR701 were higher than that of obtained from CRM601, which indicated the high lability of metals in BCR701. When compared with the sequential extraction data, it seemed that the lability of an element was positively correlated to the first step extraction fraction.

Keywords: Kinetics; Speciation; Heavy metals; EDTA; Hydroxylamine

1. Introduction

Heavy metal contamination in soils and sediments continues to be a major concern in environmental monitoring [1]. Knowing the total content of an element is no longer sufficient, as it is now generally accepted that the toxicity and mobility of heavy metal is highly dependent on their binding forms in the environment. The determination of the exact chemical species or binding forms of certain element in natural systems is challenging and often not possible, therefore the determination of broader forms depending on operationally defined sequential extraction methods can be a good compromise to give useful information. Many different extraction schemes

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have been designed to obtain elemental distributions in specific mineralogical phases in soils and sediments [2–5].

These schemes, however, have often been criticized because of the lack of selectivity of the extracting reagents; lack of uniformity in the procedures and the lack of quality control, which makes comparison of published results difficult. To partly overcome these problems, the European Commission Standard, Measurement and Testing Programme, formally known as BCR, launched a project to harmonize the single and sequential extraction procedure for the determination of extractable trace metals in soil and sediment. So far two sediments samples, namely CRM601 and BCR701, have been certificated for the BCR three-step sequential extraction scheme [5, 6]. By using the BCR method and the certified materials, the quality of the measurements can be appropriately controlled and the results compared. The interpretation of the results from this type of sequential extraction process must be based on the reagents rather than the mineral phase, due to the problems associated with the selectivity of the extracting reagents [2, 7]. In the BCR methods the three steps relate to the ''acid soluble'', ''reducible'' and ''oxidizable'' fractions respectively.

Another criticism on the sequential extraction method is that extractions are performed under equilibrium conditions (or at least close to equilibrium conditions) and therefore the information obtained is not considered to reflect the real lability and distribution of the species. To address this problem, a number of authors have carried out speciation studies based on a ''kinetic approach'' [8–10]. In these approaches, the samples are extracted with a non-selective reagent, and the concentrations of the extracted elements monitored over time. The mobility of an element can then be assessed, based on its leaching curve. By applying different modeling methods, it is also possible to obtain various kinetic parameters, which have clear physical meaning to characterize the mobility of an element. Based on their mobility, for example, species can often be classified as labile and non-labile fractions [9]. Other equally important parameters, i.e., the rate constants associated with the specified fractions, however have not yet been fully elucidated. Theoretically, the differences in the extraction rate, to a certain extent, should relate to the origins of the species, and therefore it should be possible to use the rate constant to quantify the lability of an element. As mentioned previously there has been very limited work comparing the different methods for investigating elemental lability on the same sample [11]. The aim of this work was to compare and evaluate the types of results obtained for sequential extraction and kinetic approaches on two well characterized samples, namely the two BCR reference materials developed for validation of sequential extraction methods.

2. Experimental

2.1 *Materials, reagents and instruments*

The BCR reference material CRM601 was purchased from Qmx Laboratories Limited, Essex, UK and BCR701 was purchased from European Commission-Joint Research Centre, Institute for Reference Materials and Measurements (IRMM). These reference materials were used as received and the moisture content was measured to be 3.5% for both of them. An extraction solution of $0.05\,ML^{-1}$ EDTA (Disodium ethylenediamine tetraacetic acid) was prepared by dissolving an appropriate amount of analytical grade

reagent (BDH Laboratory Supplies, Poole, UK) in water and adjusting the pH to 6.0 using a pH meter (Fisherbrand Hydrus 500, Fisher Scientific UK Ltd., Loughborough, UK). A solution of $0.5\,ML^{-1}$ hydroxylamine hydrochloride was prepared from a 98% A.C.S. reagent (Sigma-Aldrich Co. Ltd.) and the solution was acidified with nitric acid as described by the BCR procedure [6]. All the standard element solutions were prepared by dilution from a $1000 \pm 3\,\mu g\,mL^{-1}$ concentrated standard solution (Peak Performance, Qmx Laboratories Ltd., UK). High purity de-ionized water ($18\,M\Omega\,cm$ resistance) was obtained from an Elgstat UHQ PS system (Elga, High Wycombe, UK).

The element analysis in the extracts was carried out with a quadrupole inductively coupled plasma mass spectrometer (ICP-MS), from ThermoElemental, Winsford, Cheshire, UK.

2.2 *Kinetic extraction procedure*

A portion of 10 g of BCR reference material was weighed in an 800 mL beaker. An aliquot of 500 mL of extracting solution was added corresponding to a solid/solution ratio of 1 : 50 and the mixture was stirred immediately with a heavy-duty magnetic stirrer. At selected time intervals, an aliquot of 5 mL mixture was taken by a syringe and immediately filtered through a 0.45 μm cellulose acetate membrane (Millipore). Samples were collected more frequently at the first few hours of extraction, as it was considered that the change of concentration in the earlier stage was much more rapid than in the later stage. The extraction lasted for 24 h and the collected solutions were stored at 4°C prior to analysis by ICP-MS.

2.3 *Modeling method*

The kinetic parameters were estimated by using a computer software package Origin 7.0, developed by OriginLab Corporation. A user-defined two-component non-linear regression equation was chosen for the categorization of the extractable metals. The calculation of parameters was accompanied by calculation of their confidence intervals and other statistical data for the estimation of regression quality.

3. Results and discussion

3.1 *Kinetic extraction procedure*

EDTA is known to be a strong chelating agent and has been frequently utilized in kinetic studies [8–10]. It is a non-selective reagent and is capable of dissolving metals from different phases of sediment. Hydroxylamine hydrochloride is a reducing agent, and in the sequential extraction methods it is designed to release the metals associated with Fe/Mn hydroxides. Generally two different ways can be used to carry out the extraction procedure. One is to use a single sediment sample and extracting solution mixture from which aliquots are collected at different times (protocol A) and the other way is to extract independent sediment mixtures with the same ratio of sediment/extractant volume (protocol B). To save the reference materials, protocol A was used in the present work.

A major disadvantage of protocol A would be that after successive samplings, the volume of the mixture would be reduced and the intensity of agitation increased subsequently [10]. This disadvantage can largely be overcome by using the highly sensitive ICP-MS technique as the detection method, as the amount of samples taken from the extraction system can be minimized. In this work an aliquot of 5 mL sample was removed each time and it was shown to be more than enough for subsequent analysis. After 10 cycles of sampling, for example, the overall reduction in volume was no more than 10%; therefore the effect on the agitation intensity should be minimum. A concentration of $0.05\,ML^{-1}$, initial pH 6.0 and solid/solution ratio of 1 : 50 were chosen without further optimization because these conditions had previously been shown to be appropriate for kinetic studies [8–11]. For comparison purpose, the conditions for hydroxylamine hydrochloride solution was the same as used in the BCR three-step sequential extraction protocol.

3.2 *Comparison of the overall removal ratio*

On comparing the overall removal ratios between the methods it must be realized that the extraction methods are very different and that they are providing different information about metal lability as discussed below. The sequential extraction data adopted from the certificate for the BCR reference material [6] are listed in tables 1 and 2 respectively for CRM601 and BCR701. All the data has been converted into percentage expressions so that they are on similar scales. For CRM601, the data used is that obtained from the modified BCR sequential extraction protocol, to make it comparable with the results of BCR701.

The kinetic extraction data was plotted as concentration against time. Figures 1 and 2 show the results obtained from EDTA extractions of CRM601 and BCR701 respectively. Figure 3 presents the results obtained from the extraction of BCR701 by hydroxylamine hydrochloride. For comparison all the data was expressed as cumulative fractions of elements removed from the sediments. The indicative values obtained from the direct aqua regia digestion were used as the total contents [6] for subsequent calculations.

Table 1. Certified and indicative data of CRM601 with BCR three-step sequential extraction [6].

Steps	Cd	Cu	Ni	Pb	Zn
First	38.7 ± 5.8	4.6 ± 0.3	9.9 ± 1.1	0.79 ± 0.4	31.3 ± 1.6
Second	34.3 ± 4.6	31.6 ± 2.1	13.4 ± 1.6	71.2 ± 3.8	31.9 ± 2.0
Third	16.6 ± 12.4	34.2 ± 3.9	7.7 ± 1.6	6.8 ± 2.0	12.7 ± 1.3
Sum	89.6	70.4	30.1	78.8	75.9

Table 2. Certified data of BCR701 with BCR three-step sequential extraction [6].

Steps	Cd	Cu	Ni	Pb	Zn
First	62.7 ± 3.0	17.9 ± 0.6	15.0 ± 0.9	2.2 ± 0.1	45.2 ± 1.3
Second	32.2 ± 2.4	45.1 ± 1.1	25.8 ± 1.3	88.1 ± 2.1	25.1 ± 1.1
Third	2.3 ± 0.5	20.1 ± 1.5	14.9 ± 0.9	6.5 ± 1.4	10.1 ± 0.9
Sum	97.2	83.1	55.6	96.8	80.4

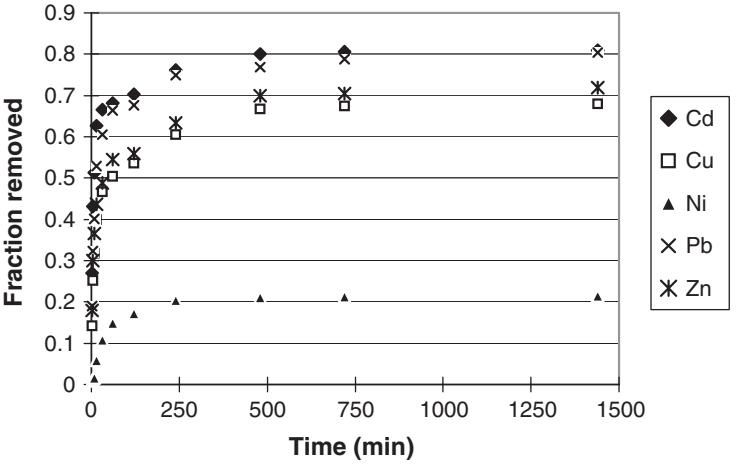

Figure 1. Extraction data obtained from CRM601 with EDTA.

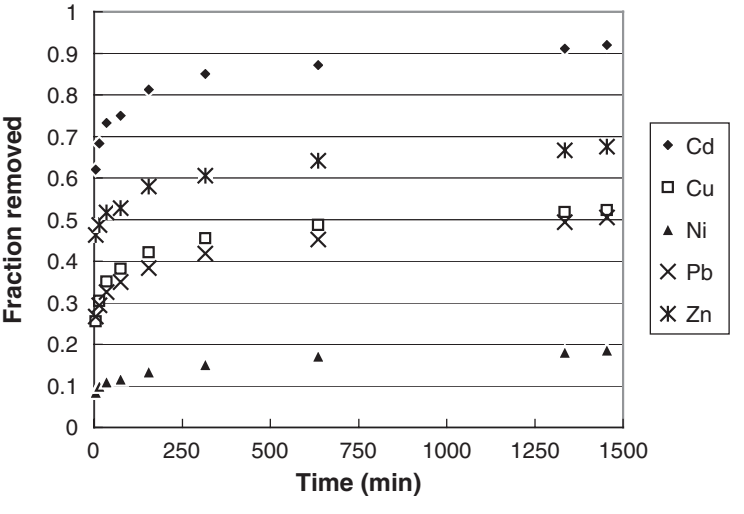

Figure 2. Extraction data obtained from BCR701 with EDTA.

CRM601: It can be seen from figure 1 that the trends were similar for all the elements, i.e. the removal ratios increased rapidly in the first few hours, and then slowed down from 8 to 24 h into the experiment. By the end of the extraction time, around 81.0% of Cd, 68.0% of Cu, 21.5% of Ni, 80.3% of Pb and 71.9% of Zn was removed from the CRM601. These figures were higher than the amounts removed by any single step of the BCR sequential extraction method, but they were, in general, approximately the same as or slightly less than the sum of the three-step extractions (see table 1). These relatively high figures also implied that as a non-selective chelating agent, EDTA extracted metals from different phases of the sediment.

BCR701: Figure 2 shows the extraction results obtained from BCR701. The trends in the extraction processes are similar to those for CRM601, but compared with CRM601

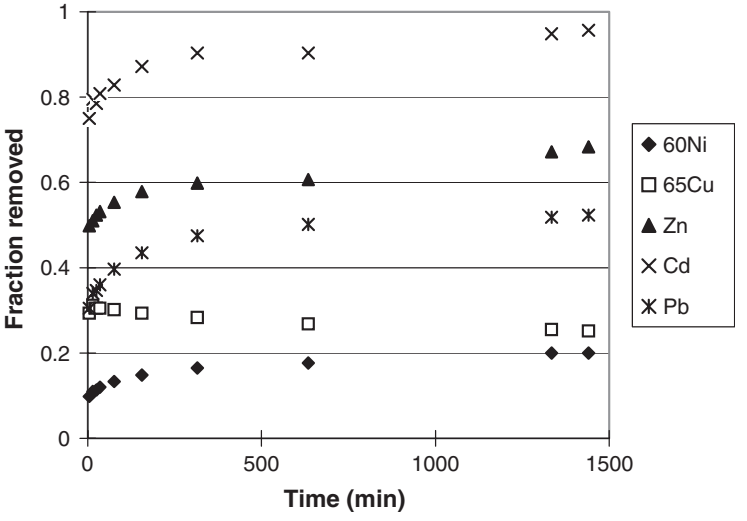

Figure 3. Extraction data obtained from BCR701 with hydroxylamine hydrochloride.

more noticeable increases in removal ratios were observed later in the extraction process, which indicated that the extraction may not be complete. By the end of the 24 h extraction, the overall removal ratios were 92.0, 52.3, 18.7, 50.6 and 67.5% respectively for Cd, Cu, Ni, Pb and Zn. It was noticed that the removal ratios for Cu, Ni and Pb were markedly lower than the sum of the three-step extraction results and also lower than the results obtain from CRM601. This may be explained by the fact that in BCR701 there are relatively large amounts of Cu, Ni and Pb associated with the reducible fractions, to which the chelating agent may become less accessible. Extraction with hydroxylamine hydrochloride was then carried out on the BCR701. The results are presented in figure 3.

As it can be seen that the overall removal ratios were, in general, greater than those obtained from EDTA, this can be contributed to the strong acidity and the reducing effect of hydroxylamine hydrochloride solution. The removal ratios for Cd, Ni, Pb and Zn reached 95.7, 20.0, 52.4 and 68.5% respectively. Cu was an exception, as the extraction curve with hydroxylamine hydrochloride behaved quite uniquely. It culminated at 15 min with 31.1% of Cu being removed from the sediment, and then this figure decreased gradually to 25.2% at the end of the extraction process. This peculiar trend may be explained by a re-deposition phenomenon, i.e., the released Cu, being reduced to one plus cation, may experience a precipitation reaction with chloride in solution to form copper (I) chloride and stay in the solid phase.

3.3 *Kinetic modeling*

As mentioned earlier, by applying different modeling methods to the extraction data, it is also possible to obtain various kinetic parameters to further characterize the mobility of an element. One of the frequently utilized models is given as [8, 9, 11],

$$Y = A_1(1 - e^{-l_1 t}) + A_2(1 - e^{-l_2 t})$$

Table 3. Non-linear regression parameters and the statistical test results.

Element		Fitted parameters				Statistics	
		A_1	A_2	k_1	k_2	R_{sqr}	Chi^*_{sqr}
CRM601	Cd	0.6154 ± 0.0191	0.1938 ± 0.0204	0.2726 ± 0.0228	0.0059 ± 0.0018	0.9911	3.8×10^{-4}
	Cu	0.4127 ± 0.0169	0.2679 ± 0.0173	0.1966 ± 0.0192	0.0056 ± 0.0010	0.9952	2.3×10^{-4}
	Ni	0.1620 ± 0.0616	0.0528 ± 0.0584	0.0266 ± 0.0087	0.0054 ± 0.0066	0.9936	7.0×10^{-5}
	Pb	0.5474 ± 0.0327	0.2417 ± 0.0323	0.1857 ± 0.0234	0.0076 ± 0.0024	0.9906	5.8×10^{-4}
	Zn	0.4369 ± 0.0177	0.2775 ± 0.0188	0.2511 ± 0.0270	0.0055 ± 0.0011	0.9928	3.2×10^{-4}
BCR701	Cd	0.6852 ± 0.0155	0.2212 ± 0.0172	0.4558 ± 0.0620	0.0047 ± 0.0010	0.9835	2.9×10^{-4}
	Cu	0.3140 ± 0.0137	0.2000 ± 0.0150	0.3130 ± 0.0561	0.0044 ± 0.0009	0.9927	2.1×10^{-4}
	Ni	0.0987 ± 0.0023	0.0857 ± 0.0028	0.3794 ± 0.0468	0.0032 ± 0.0003	0.9964	8.0×10^{-6}
	Pb	0.3539 ± 0.0109	0.1410 ± 0.0125	0.3909 ± 0.0631	0.0038 ± 0.0010	0.9908	1.6×10^{-4}
	Zn	0.4871 ± 0.0088	0.1810 ± 0.0103	0.5734 ± 0.0963	0.0037 ± 0.0006	0.9886	1.1×10^{-4}

*Chi_{sqr} in actual value is reduced Chi^2.

where Y is the cumulative fraction removed from the solid matrix and t is the extraction time. A_1 and A_2 represent the labile and non-labile fractions respectively and k_1 and k_2 are rate constants associated with them.

The kinetic parameters obtained from the extraction data of CRM601 and BCR701 are given in table 3, as well as the statistics associated with the non-linear regressions. By using this model, the extracted metals were readily classified into two categories i.e., the labile and the non-labile fraction. A great advantage of modeling the extraction curve is that the differences in kinetic behavior can be quantitatively assessed by the parameters obtained. These differences are often not obvious by visual inspection of the extraction curves.

In both samples Cd exhibited a high lability, as in both cases the labile fractions accounted for more than 60% of the total contents and their rate constants were also high. This is especially evident for Cd in BCR701, where 68.5% of Cd was classified as labile and its rate constant was 0.4558. When these figures were substituted into the model equation, the result clearly showed that only 21 min were needed to completely leach the labile fraction out of the solid matrix. Similarly, the time needed to leach the labile fraction from CRM601 would be 41 min. For the non-labile fraction, the rate constants were similar, which suggests that the non-labile Cd in the two samples may come from similar mineralogical phases. The very low value for the rate constant means that a long time would be required to complete the extraction of the non-labile fraction from the sediments. For example, in the case of BCR701, the calculated time is 46 h. It is interesting to look at the sequential extraction data in table 1 and 2. The major difference seen in the fraction of the first step extraction may be accounted for by the different kinetics.

As mentioned earlier (section 3.2), greater percentages of Cu, Ni and Pb were removed from CRM601 than from BCR701. The regression data also reflected these facts, i.e., A_1 obtained from CRM601 were greater than that obtained from BCR701. For the rate constant k_1, however, an opposite trend was seen, i.e., the k_1 obtained from BCR701 was greater in value. These results mean that although Cu, Ni and Pb have larger labile fractions in CRM601, their lability was lower than in BCR701 and it would therefore take longer to leach them from CRM601.

Ni behaved quite differently in the two sediments. In CRM601, k_1 was very small. It can be calculated that 8 h would be needed to leach out this "labile" fraction,

while for the same fraction in BCR701, only 5 min is needed. The rate constant clearly demonstrated the significance of the lability. In kinetic speciation, it is therefore essential to not only classify the fractions but also to provide the associated rate constants.

Similar amounts of Zn were removed from both sediments, and their kinetic parameters also showed a similar leaching pattern. When the rate constants were considered, however, it could be found that the lability of Zn in BCR701 was greater than that in CRM601. When compared with the sequential extraction data, the greater fraction of first step in BCR701 may attribute to the differences in kinetics.

From the above discussion, it can be concluded that the metals in BCR701 are generally more labile than those in CRM601, although in CRM601 more fractions of Cu, Ni and Pb are classified as labile. It is important to emphasize here that it is the rate constants that should be used to assess the lability of an element.

4. Conclusions

The lability of metals in two BCR reference materials has been evaluated quantitatively by a kinetic approach. Generally more metals can be removed from CRM601 than from BCR701 with EDTA as an extractant. For sample BCR701, acidified hydroxylamine hydrochloride was shown to be more efficient than EDTA for the extraction of metals. By applying a kinetic model, all the elements in the study could be readily classified as labile and non-labile fractions. The rate constant calculated from the kinetic model allowed the lability of each element to be easily assessed and compared with other elements or other samples. The kinetic approach is a relatively simple and rapid method that produces convincing information about elemental lability in a solid matrix. Compared with the sequential extraction procedure, only one extractant and one step are generally required for the experiment, therefore the likelihood to incur experimental error is minimized. Potentially this method would be very useful in determining the extraction time, if for example, a soil (or sediment) washing is to be carried out.

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