

## Evaluation of the BCR sequential extraction procedure applied for two unpolluted Spanish soils

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**“Capsule”:** *The sequential extraction procedure of BCR is suitable for As, Pb and Cd at low concentrations, but not for Cu, Co, Cr, Zn and Ni.*

### Abstract

The procedure of BCR sequential extraction has been applied to five samples from two unpolluted soils in southern Spain. Total concentrations of different elements have been calculated as the sum of the three fractions of BCR and the residue has been measured for each. Also, a total analysis based on INAA or total-digestion techniques has been performed for the same samples. BCR and total analysis closely agreed for As, Pb and Cd. For Cu, Co, Cr and Zn the comparison of the results did not provide definitive conclusions concerning the capability of BCR in measuring total concentrations. On the other hand, in these cases, a certain correlation was found between the concentrations measured and some soil characteristics, especially the clay, organic-matter and CaCO<sub>3</sub> contents. BCR proved incapable of providing accurate measurements for Ni.

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### 1. Introduction

Selective extraction methods for trace metals have been widely studied: Tessier et al. (1979); Gibson and Farmer (1986); Miller et al. (1986) and Oughton et al. (1992), among others. Some authors have compared different extraction methods for metals or have partially modified existing ones: Kheboian and Bauer (1987); Rauret et al. (1989); López-Sánchez et al. (1993); Fiedler et al. (1994); Mester et al. (1998).

In principle, the determination of element concentrations using extraction methods shows greater uncertainties than do the procedures in which their total contents are determined in a direct manner. This is due to: (1) the difficulties in isolating the compounds to be studied from their substrates; (2) the possibility of upsetting the

equilibrium between the different chemical species present in the system; (3) the inadequate analytical sensitivity of some of the techniques, especially when trace elements are found at very low concentrations; and (4) the frequent lack of certified reference materials (Pickering, 1995).

The proposal of the European Community Bureau of Reference, usually called the BCR method (Ure et al., 1992), seeks to minimize errors in the treatment and analysis of samples, to identify the most appropriate analytic procedure and to supply reference materials for comparisons of the results between different laboratories. This method appears to be more operationally effective than others proposed previously, such as that of Tessier (Tessier et al., 1979). Nevertheless, the dissolution or selective destruction of the soil components seems to be implicit in any sequential extraction technique, as does the non-specificity of the reagent or the possibility of the redistribution of metals during the extraction (Sheppard and Stephenson, 1997).

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Recent years have shown growing interest in the BCR method, both in polluted as well as non-polluted soils (Ure et al., 1993; Sahuquillo et al., 1999; Barona et al., 1999; Száková et al., 1999). The method has been used not only in laboratory experiments, with mineralogically uniform samples (humic acids, calcium carbonate, iron oxides or manganese, illite, montmorillonite, etc.) and with controlled quantities of added metals (Whalley and Grant, 1994), but also in natural substrates, fundamentally sediments from estuaries (Davidson et al., 1994; Thomas et al., 1994; Fiedler et al., 1994; Sahuquillo et al., 2002).

The use of simple substrates eliminates the problem of the redistribution of the metal into the constituents of the substrate (Belzile et al., 1989), and the samples reach equilibrium better in sea-water solutions, such as the estuary substrates (Whalley and Grant, 1994).

In the present study, we test the suitability and applicability of this procedure for the evaluation of the behaviour of 11 elements (As, Cd, Co, Cu, Cr, Ni, Se, Sn, Pb, Bi and Zn) in five horizons from two uncontaminated soils.

## 2. Materials and methods

### 2.1. Analytical methods

The five soil samples analysed belong to two profiles from Campillos (S Spain). The soils are classified according to the FAO (1998) as Haplic Calcisol and Luvic Calcisol. The macromorphological and analytical characteristics, given in Aguilar et al. (2002), are summarized in Table 1. The soil samples were submitted to different treatments:

- A total analysis performed by Activation Laboratories Ltd. (Ontario, Canada). The contents in As, Co, Cr, Se and Sn were determined with the INAA (Instrumental Neutron Activation Analysis) technique, one of the most sensitive methods for measuring trace elements (Hoffman, 1992). For the other elements, soil samples, finely ground (<0.05 mm), were digested in strong acids (HF,

HClO<sub>4</sub>, HNO<sub>3</sub> and HCl) at 200 °C to fuming and were diluted with dilute aqua regia. The solutions were read on a simultaneous Jarrell Ash ICP spectrometer or a Perkin Elmer OPTIMA 3000 ICP. We have used these results as reference measurements for our analysis.

- A BCR sequential extraction with diluted acetic acid (0.1 mol l<sup>-1</sup>), a reducing agent (hydroxylammonium chloride 0.5 mol l<sup>-1</sup>) and an oxidant (hydrogen peroxide 8.8 mol l<sup>-1</sup>). The measurements were made at the Instrumentation Center of the University of Granada. An ICP/MS mass was used to determine the concentrations in µg/l of the solutions of each of the three steps of the BCR method, as well as that of the acid attack of the residue. This latter determination was performed in a way similar to that described for the total analysis. However, we considered two different procedures in the sample dilution after drying, thus having two replicates of the samples. In the first one (Residue A) no reference volume was considered and the dilution factor was 10.25. In the second one (Residue B) the sample was diluted to a reference volume using a dilution factor of 50. The comparison with the total analysis results could help us to elucidate which one of the two procedures is more correct.

### 2.2. Statistical methodology

As previously stated, our aim was to test the BCR technique for the determination of the concentration of the 11 elements mentioned above in five soil samples, labelled 3Ah, 3Bwk, 6Ap, 6Bt and 6Bw. To do so, we first calculated the BCR total concentration,  $C^\alpha$ , of each element in each soil according to the following expression:

$$C^\alpha = \sum_{i=1}^3 c_i + r^\alpha \quad (1)$$

where  $\{c_i, i = 1, 2, 3\}$  represents the concentrations determined in each of the three BCR steps, and  $r^\alpha$  signifies that of the residue. The superindex  $\alpha$  refers to the two residues (A and B) described above. The corresponding uncertainties,  $\sigma(C^\alpha)$ , were calculated as the quadratic sum of the respective errors of the concentrations resulting from each of the BCR steps and the residue:

$$\sigma(C^\alpha) = \sqrt{\sum_{i=1}^3 [\sigma(c_i)]^2 + [\sigma(r^\alpha)]^2} \quad (2)$$

The resulting values were compared to the reference values provided by the total analysis, which gives us the total concentrations,  $T$ , as well as the corresponding uncertainties,  $\sigma(T)$ , for each element in each soil sample.

Table 1  
Values (in %) for the composition of the five horizons considered

Composition of the horizons	Clay	CaCO <sub>3</sub>	pH	Fine silt and clay (<0.02 mm)	Organic matter	
Horizons	Error (%)	5.0	2.0	0.2	5.0	0.2
3Ah		47.4	11.4	8.0	76.4	2.71
3Bwk		57.6	21.7	8.0	87.3	1.43
6Ap		51.5	9.6	8.2	73.8	2.57
6Bw		51.7	7.6	8.1	85.3	1.07
6Bt		65.9	7.5	8.1	71.4	1.71

In addition to the direct comparison of the values found, we have calculated, for each element and each soil, the quantity

$$\gamma = \frac{C^\alpha + T}{\sqrt{[\sigma(C^\alpha)]^2 + [\sigma(T)]^2}} \quad (3)$$

It can be shown (see Frödesen et al., 1979) that if the total concentrations determined with the two methods derive from the same parental distribution, the variable  $\gamma$  should be a Gaussian distribution centred at 0 with variance 1.

Finally, for each step of the BCR method we calculated the correlations between the concentrations of each element and the soil characteristics listed in Table 1, by means of the Pearson's linear correlation coefficient (Press et al., 1992):

$$r_i = \frac{\sum(c_i - \bar{c})(v - \bar{v})}{\sqrt{\sum(c_i - \bar{c})^2} \sqrt{(v - \bar{v})^2}} \quad (4)$$

where the sums for the five soils analysed,  $\bar{c}$ , is the mean of the values  $c_i$  for these soils,  $v$  refers to the soil characteristics and  $\bar{v}$  is the corresponding mean value.

Also, the uncertainty of these correlation coefficients was determined following a Monte Carlo technique. For each  $c_i$  value, we generated a random value according to the Gaussian distribution centred on it, with variance  $[\sigma(c_i)]^2$ . The same procedure was performed for each  $v$  value. This gave new sets of values  $c_i^{(k)}$  and  $v^{(k)}$ , for the five soils considered. By repeatedly using Eq. (4), we obtained a set of values  $\{r_i^{(k)}, k = 1, \dots, N\}$  while the uncertainty of the original linear coefficient  $r_i$  is given by the standard deviation of these  $N$  values. We verified that  $N = 1000$  was adequate for convergence in the results.

The various statistical methods used are documented in Press et al. (1992) and Frödesen et al. (1979). To

perform the calculations, we prepared a series of programs in FORTRAN language, especially designed for each particular case. The programs were run on a PC under the Linux operating system.

### 3. Results and discussion

#### 3.1. Validity of the BCR method for the elements studied

First, we analysed the results for the total concentrations of the different elements considered.

In the analysis, we did not consider Se, since we found no concentrations of this element, within the error limits, either in the total-analysis measurements or in any of the steps of the BCR.

The reference measurements indicated that both Sn and Bi were absent from the samples analysed. Nevertheless, we considered them because the concentrations found in the case of the BCR fractionated extraction and/or the acid attack were above the minimum measurement levels.

Tables 2–6 show the concentrations, in mg/kg, found with the two methods. The BCR values were derived from the concentrations in  $\mu\text{g/l}$ , taking into account that the dilution factors were 4 for the first two BCR steps and 10 for the third one.

To evaluate the validity of the BCR extraction procedure for all elements considered, we first compared the values of the total concentrations given by this procedure with the total reference concentrations. This comparison is made in Fig. 1, where each panel corresponds to one of the ten elements under consideration. In each panel the results for the five soil samples studied are shown separately. Experimental points correspond to the BCR (A and B) concentrations. The error bars correspond to  $1\sigma$  (solid lines) and  $2\sigma$  (broken lines),  $\sigma$  being the error given in Tables 2–6. The reference values

Table 2

Values for the concentrations,  $C^\alpha$ , in mg/kg, of the different elements obtained in the three steps of the BCR and in the acid attacks, as well as the values for the total concentrations in the 3Ah horizon

Concentration (mg/kg)	Total INAA	Total acid attacks	BCR			Residue A	Total A	Residue B	Total B
			Step 1	Step 2	Step 3				
As	10.2(5)		0.8(2)	2.1(6)	0.8(2)	11(3)	15(3)	25(8)	29(8)
Co	16(1)		2.8(3)	2.6(3)	2.4(2)	4.1(4)	11.9(6)	18(2)	25(2)
Cr	70(5)		1.2(1)	14(1)	3.4(3)	47(4)	66(4)	790(40)	800(40)
Sn	0(100)		4(1)	3(1)	12(4)	0.00(3)	20(4)	90(30)	110(30)
Bi		0(10)	0.12(1)	0.000(4)	0.50(5)	0.00(1)	0.62(5)	4.5(5)	5.1(5)
Cd		0.5(5)	0.000(4)	0.000(4)	0.40(4)	1.3(1)	1.7(1)	0.50(5)	0.90(6)
Cu		34(1)	1.0(1)	0.000(4)	0.00(1)	17(2)	18(2)	0.00(5)	1.0(1)
Ni		35(1)	7.3(7)	4.1(4)	17(2)	22(2)	50(3)	190(20)	210(20)
Pb		20(5)	0.000(8)	7(1)	2.3(5)	4.1(8)	13(2)	13(3)	22(3)
Zn		44(1)	0.000(4)	0.000(4)	0.00(1)	50(4)	50(4)	1970(80)	1970(80)

The values in parenthesis give the uncertainties (corresponding to the last significant figure) such as, for example, 10.2(5) means  $10.2 \pm 0.5$ .

Table 3

Values for the concentrations,  $C^{\alpha}$ , in mg/kg, of the different elements obtained in the three steps of the BCR and in the acid attacks, as well as the values for the total concentrations in the 3Bwk horizon

3Bwk									
Concentration (mg/kg)	Total INAA	Total acid attacks	BCR			Residue A	Total A	Residue B	Total B
			Step 1	Step 2	Step 3				
As	10.1(5)		0.4(1)	2.3(7)	0.00(3)	8(3)	11(3)	0.0(2)	2.7(7)
Co	15(1)		2.8(3)	1.6(2)	1.4(1)	4.3(4)	10.1(6)	0.00(5)	5.8(4)
Cr	77(5)		0.000(4)	16(1)	0.60(6)	51(4)	68(4)	0.00(5)	17(1)
Sn	0(100)		4(2)	2.7(8)	13(4)	0.00(3)	20(4)	0.0(2)	20(4)
Bi		0(10)	0.32(3)	0.040(4)	0.20(2)	0.00(1)	0.56(4)	0.00(5)	0.56(6)
Cd		0.0(5)	0.000(4)	0.040(4)	0.10(1)	0.10(1)	0.24(2)	0.00(5)	0.14(5)
Cu		35(1)	0.000(4)	0.000(4)	0.00(1)	17(2)	17(2)	0.00(5)	0.00(5)
Ni		39(1)	5.2(5)	4.2(4)	7.7(8)	57(4)	75(4)	0.00(5)	17(1)
Pb		22(5)	0.000(8)	3.5(7)	3.9(8)	2.6(5)	10(1)	0.0(1)	7(1)
Zn		51(1)	0.000(4)	0.000(4)	0.00(1)	52(4)	52(4)	0.00(5)	0.00(5)

The values in parenthesis give the uncertainties (corresponding to the last significant figure) such as, for example, 10.1(5) means  $10.1 \pm 0.5$ .

are represented in the figure as shaded regions. The dark region corresponds to the total concentration value  $\pm 1\sigma$  and the lighter region to the same total value  $\pm 2\sigma$ .

As can be seen, the agreement, within the uncertainties, between the total concentrations measured with BCR and the reference ones is reasonable only for some elements and/or horizons. This can be seen also in Table 7, where the variable  $\gamma$ , calculated according to Eq. (3), is shown for the different elements and soils. As mentioned above, this quantity should be a Gaussian distribution centred at 0 and with  $\sigma = 1$ , and thus we marked (shadowed cells) those cases with  $|\gamma| \leq 3$ , which we assume to be representative of a reasonable agreement between both methods.

In case of As, we found that BCR is valid for all five soil samples. In fact, one of the two BCR results (A or B) provides a  $|\gamma|$  value lower than 1.4. In our analysis, we found the greatest concentration of this element in the residual fraction in all the horizons studied (see Tables 2–6), a result which agrees with the findings of Dhoun and Evans (1998). In addition, these authors indicated

that the values found in the second step of the sequential extraction can present an error associated with the interference between Cl and As and, therefore, they suggest replacing hydroxyammonium chloride by hydroxyammonium sulphate for more accurate results. In our study, the highest quantity of As, after that in the residue, appeared in the second BCR step; moreover, the value calculated was probably lower than the actual one, because, as suggested in some works, 80% of the As in the soils is associated with Fe and Al oxides, and the mobility of this element in soils is inversely proportional to the addition time and to the Fe and Al content in the substrate (Vangronsveld and Cunningham, 1998; Thornton and Farago, 1997; Kabata-Pendias, 2001; Simón et al., 2001). In addition, calcium carbonate strongly immobilizes As, as demonstrated in experiments by Dorronsoro et al. (2002) in soil remediation of the Guadiamar Basin after the toxic spill of Aznalcóllar.

The BCR results for Co agreed with the reference total concentrations, within the experimental uncertainties, for all the horizons of profile 6, but not for those of

Table 4

Values for the concentrations,  $C^{\alpha}$ , in mg/kg, of the different elements obtained in the three steps of the BCR and in the acid attacks, as well as the values for the total concentrations in the 6Ap horizon

6Ap									
Concentration (mg/kg)	Total INAA	Total acid attacks	BCR			Residue A	Total A	Residue B	Total B
			Step 1	Step 2	Step 3				
As	12.1(5)		0.4(1)	2.2(6)	1.1(3)	20(6)	24(6)	14(4)	18(4)
Co	23(1)		0.72(7)	4.8(5)	1.2(1)	9.0(9)	16(1)	18(2)	24(2)
Cr	123(5)		1.6(2)	14(1)	0.00(1)	143(7)	159(7)	170(10)	190(10)
Sn	0(100)		5(1)	2.8(8)	12(4)	0.00(3)	20(4)	100(30)	120(30)
Bi		0(10)	0.080(8)	0.16(2)	0.20(2)	0.10(1)	0.54(3)	8.5(9)	8.9(9)
Cd		0.0(5)	0.000(4)	0.000(4)	0.00(1)	1.1(1)	1.1(1)	2.0(2)	2.0(2)
Cu		36(1)	0.000(4)	0.000(4)	0.00(1)	28(3)	28(3)	0.00(5)	0.00(5)
Ni		52(1)	3.6(4)	5.4(5)	5.1(5)	89(5)	103(5)	110(10)	120(10)
Pb		31(5)	0.000(8)	4.6(9)	5(1)	4.1(8)	14(2)	18(4)	28(4)
Zn		65(1)	0.000(4)	0.000(4)	0.00(1)	105(5)	105(5)	0.00(5)	0.00(5)

The values in parenthesis give the uncertainties (corresponding to the last significant figure) such as, for example, 12.1(5) means  $12.1 \pm 0.5$ .

Table 5

Values for the concentrations,  $C^x$ , in mg/kg, of the different elements obtained in the three steps of the BCR and in the acid attacks, as well as the values for the total concentrations in the 6Bt horizon

Concentration (mg/kg)	Total INAA	Total acid attacks	BCR			Residue A	Total A	Residue B	Total B
			Step 1	Step 2	Step 3				
			As	14.1(5)					
Co	25(1)		0.76(8)	6.6(6)	2.3(2)	1.5(2)	11.2(7)	16(2)	25(2)
Cr	138(5)		0.64(6)	13(1)	3.3(3)	18(2)	35(2)	170(10)	180(10)
Sn	0(100)		6(2)	3(1)	12(3)	0.00(3)	20(4)	80(20)	100(20)
Bi		0(10)	0.080(8)	0.040(4)	0.30(3)	0.00(1)	0.42(3)	4.5(5)	4.9(5)
Cd		0.5(5)	0.000(4)	0.000(4)	0.00(1)	1.3(1)	1.3(1)	1.0(1)	1.0(1)
Cu		36(1)	0.000(4)	0.000(4)	0.00(1)	28(3)	28(3)	0.00(5)	0.00(5)
Ni		62(1)	6.6(6)	8.8(8)	14(1)	12(1)	41(2)	120(10)	150(10)
Pb		24(5)	0.000(8)	5(1)	5(1)	37(6)	48(7)	6(1)	16(2)
Zn		72(1)	0.000(4)	0.000(4)	0.00(1)	1360(30)	1360(30)	0.00(5)	0.00(5)

The values in parenthesis give the uncertainties (corresponding to the last significant figure) such as, for example, 14.1(5) means  $14.1 \pm 0.5$ .

profile 3. The low concentrations in this profile may have caused these negative results. Tokalioglu et al. (2000), applying the BCR method to sediments of Turkey, arrived at the same conclusion with respect to Co, since small concentrations of this element could cause high relative errors. On the other hand, these authors indicated that roughly 50% of the Co is recovered in the third step, probably as CoS, while 35% is found in the residue. Our results differ notably. In fact, only about 9% of the total was recovered in the third BCR step, while around 20% was found in the second step (reducible fraction) and about 72% in the residue.

For Cr, the BCR results were consistent with the reference ones for the two horizons of profile 3, and for two horizons of profile 6, though the horizon 6Bt was at the limit considered ( $\gamma = 2.983$ ). In case of the horizon 6Ap, the BCR did not work, despite that the total content in this latter horizon was appreciably higher. The inability of the BCR method to account for the sequential extraction of the Cr has been documented by

different authors. Thus, Fiedler et al. (1994) found concentrations of Cd, Cr, Cu and Pb only in the third BCR step, with an error higher than 10%, and thus they could not demonstrate the stability of the method for these elements. Thomas et al. (1994) concluded that the high concentrations of the Cr present in the samples studied, in relation to the other elements present, provoked antagonistic effects which were the cause of error in this element, the same also affecting Cu and Ni. Gómez et al. (2000) found high interference matrices in the determination of Cd and Cr, which these authors explained by the high salt content in the extract solutions. Davidson et al. (1998) also reported results for Cr in the residual fraction, but cited the work of Coetzee et al. (1995) who, working with reference substrates, extracted Cr in the third step of the BCR. In our soils, the highest concentrations of Cr were found in the residual fraction and additional small quantities were obtained in the three BCR steps, especially in the second extraction.

Table 6

Values for the concentrations,  $C^x$ , in mg/kg, of the different elements obtained in the three steps of the BCR and in the acid attacks, as well as the values for the total concentrations in the 6Bw horizon

Concentration (mg/kg)	Total INAA	Total acid attack	BCR			Residue A	Total A	Residue B	Total B
			Step 1	Step 2	Step 3				
			As	13.7(5)					
Co	29(1)		0.72(7)	4.7(5)	2.3(2)	6.9(7)	14.6(9)	17(2)	25(2)
Cr	120(5)		0.76(8)	12(1)	4.3(4)	93(5)	110(5)	550(30)	570(30)
Sn	0(100)		5(1)	3.2(9)	13(4)	0.00(3)	21(4)	90(30)	110(30)
Bi		0(10)	0.12(1)	0.000(4)	0.80(8)	0.21(2)	1.13(8)	4.5(5)	5.4(5)
Cd		0.0(5)	0.16(2)	0.040(4)	0.00(1)	0.92(9)	1.12(9)	0.00(5)	0.20(5)
Cu		37(1)	0.000(4)	0.000(4)	0.00(1)	45(4)	45(4)	0.00(5)	0.00(5)
Ni		50(1)	2.4(2)	4.6(5)	10(1)	71(5)	88(5)	130(10)	150(10)
Pb		33(5)	0.000(8)	4.4(9)	1.5(3)	4.7(9)	11(1)	11(2)	16(2)
Zn		66(1)	0.000(4)	0.000(4)	0.00(1)	133(7)	133(7)	1000(50)	1000(50)

The values in parenthesis give the uncertainties (corresponding to the last significant figure) such as, for example, 13.7(5) means  $13.7 \pm 0.5$ .

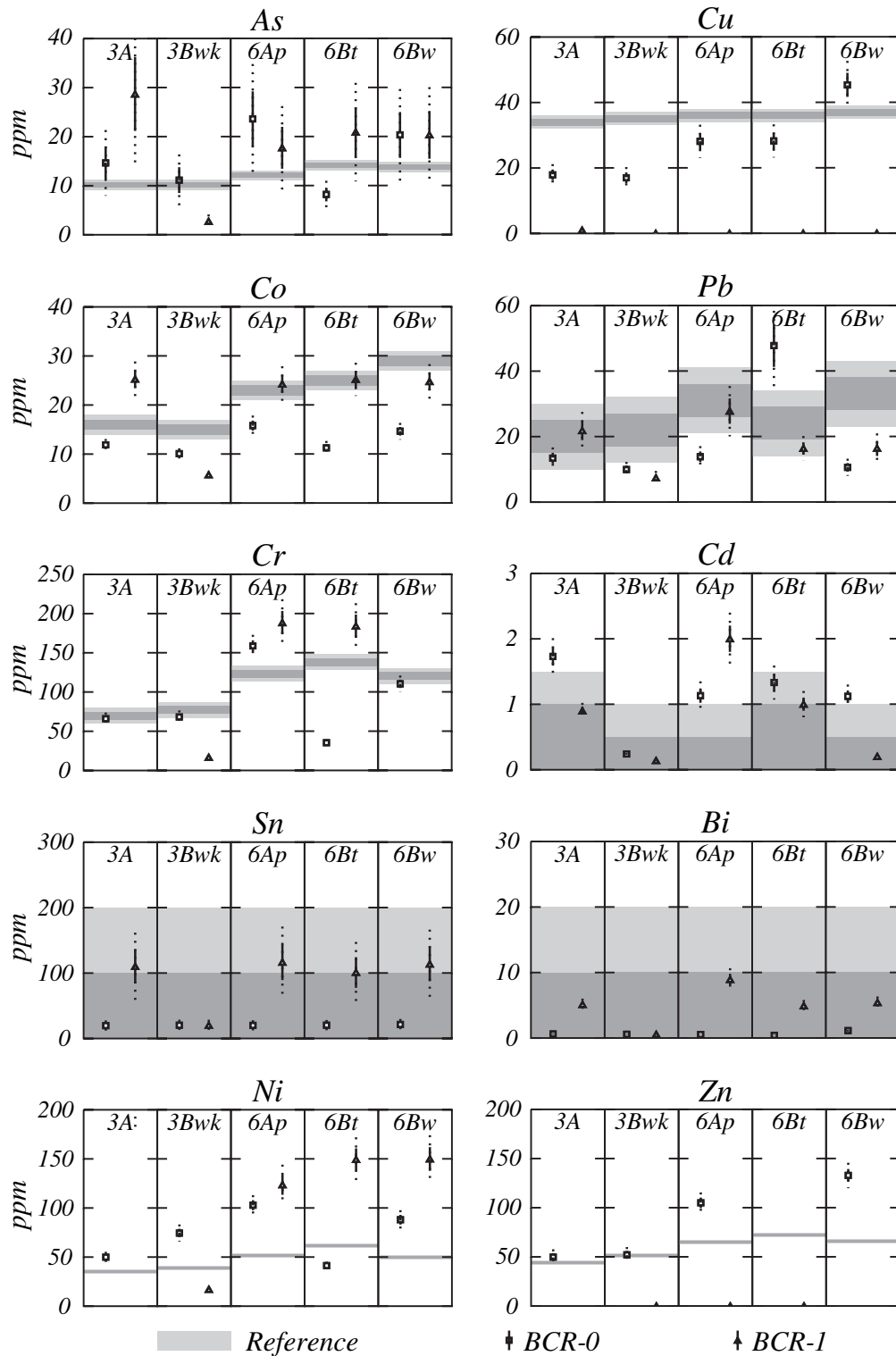


Fig. 1. Comparison between the total reference concentrations (shaded areas) and those from the BCR method for the two cases of acid attack (experimental points). The dark and light areas represent the intervals  $1\sigma$  and  $2\sigma$ , respectively. The experimental points include the intervals of error of  $1\sigma$  (solid line) and  $2\sigma$  (broken line).

The case of Pb, under the BCR method proved similar to that of Cr, horizon 6Bw being the only one for which the results did not agree at all with the reference concentrations. For Cd, the BCR agreed with the

reference method for all the horizons studied, though for the 6Ap the value  $\gamma = 2.199$  was found. For these two elements, the low concentrations in the samples analysed, as noted by Thomas et al. (1994) and Fiedler

et al. (1994), or the interference matrices, as observed by Davidson et al. (1998), can notably alter the findings of the BCR method.

The behaviour of Cu resembled that of Co, in that the BCR and reference total concentrations agreed only for the horizons of profile 6, though the values for  $|\gamma|$  were higher than 2. In these horizons, all the Cu found in our analysis was in the residual fraction, contrary to the results of Davidson et al. (1994), who, working with concentrations similar to ours, extracted it bonded mainly to the oxidizable fraction, probably forming organo-metallic complexes.

For Zn, in contrast to Cu, the BCR agreed with the total analysis for the two horizons of profile 3, but not for those of profile 6. However, as in the case of Cu, Zn was extracted exclusively in the residual fraction, a result which does match that of Davidson et al. (1994), who found Zn concentrations in all three steps of the BCR method.

The two elements for which the BCR results best agree with the reference total concentrations were Sn and Bi. It bears noting again that, for these two elements, the reference measurements were lower than the experimental uncertainties, while the concentrations found were above these uncertainties in the case of the fractionated extraction.

Finally, Ni was not extracted adequately by the BCR method. Other authors have also reported problems in determining this element. Fiedler et al. (1994) reported chance errors in the analysis process; Thomas et al. (1994) ascribed such problems to interference with other elements such as Cr; and Sahuquillo et al. (1999)

proposed modifying the method by adjusting the pH of the extractant solutions.

According to the  $\gamma$  values presented in Table 7, we conclude that the validity of the BCR method depends strongly on the elements analysed and also shows a certain dependence on the particular soil sample studied. Only in a few cases does this methodology of fractionated extraction, as used, provide results that agree with those of the reference method, within experimental uncertainties. However, it is remarkable, for example, that the BCR values for Ni completely disagreed with reference ones, and, for Zn and Cu, agreement was found only for two and three horizons, respectively.

### 3.2. Correlations between the concentrations measured in the BCR steps and the soil characteristics

Next, we analysed the possible correlations between the soil characteristics and the concentrations of the elements studied, extracted in the three steps of the BCR and the acid attack.

In view of the results of the foregoing section, it is clear that not all the values provided by the BCR method are reliable. Therefore, these correlations were studied only for those cases in which  $|\gamma|$  remained lower than 3. These cases are indicated in Table 7. When the two values, A and B, fulfilled this condition for a single element and horizon, we considered only the better one, that is, that with the lower value of  $|\gamma|$ .

The linear correlation coefficient in Eq. (4) found in these cases is shown in Table 8. We italicized the situations in which the coefficient was greater than 0.8. The

Table 7  
Values of the parameter  $\gamma$  calculated according to Eq. (3) for the two total (A and B) BCR procedures

$\gamma$	3Ah		3Bwk		6Ap		6Bt		6Bw	
	A	B	A	B	A	B	A	B	A	B
As	1.314	2.447	0.385	-8.475	2.043	1.304	-3.995	1.345	1.407	1.353
Co	-3.537	4.484	-4.315	-8.713	-5.027	0.607	-11.269	0.102	-10.886	-2.087
Cr	-0.653	19.257	-1.366	-11.643	4.122	4.147	-18.935	2.983	-1.341	16.124
Sn	0.197	1.067	0.203	0.203	0.2	1.124	0.203	0.982	0.212	1.1
Bi	0.062	0.511	0.056	0.056	0.054	0.891	0.042	0.492	0.112	0.541
Cd	2.374	0.794	0.486	0.279	2.199	3.714	1.609	0.98	2.207	0.398
Cu	-8.402	-32.795	-9.367	-34.955	-2.902	-35.953	-2.857	-35.953	2.183	-36.952
Ni	5.144	11.248	7.881	-15.362	9.658	6.95	-9.006	7.754	7.605	8.208
Pb	-1.254	0.312	-2.349	-2.862	-3.269	-0.516	2.887	-1.43	-4.337	-3.025
Zn	1.44	24.296	0.234	-50.934	7.491	-64.916	47.331	-71.907	10.139	20.001

The cases with  $|\gamma| \leq 3$  are marked. Those marked in dark are considered to study the correlations.

Table 8

Values of the correlation coefficient between the concentrations obtained in BCR step 1 and the characteristics of the composition of the soils considered

	Element	Clay	CaCO <sub>3</sub>	pH	Fine silt and clay (<0.02 m)	Organic matter
BCR step 1	As	-0.16(5)	-0.5(3)	-0.4(4)	-0.2(4)	0.1(4)
	Co	1.0(8)	-0.5(8)	-0.5(8)	1.0(8)	-0.8(8)
	Cr	-0.5(2)	-0.73(7)	0.1(2)	-0.7(2)	0.69(7)
	Sn	0.7(6)	-0.7(5)	0.5(5)	0.0(5)	-0.5(5)
	Bi	0.1(2)	0.96(2)	0.64(8)	0.6(2)	-0.30(5)
	Cd	-0.2(2)	-0.38(3)	0.1(1)	-0.6(2)	-0.15(4)
BCR step 2	As	-0.6(5)	0.5(6)	-0.1(6)	0.3(6)	0.3(5)
	Co	1.00(8)	-0.5(3)	-0.5(3)	1.0(1)	-0.8(2)
	Cr	-0.0(4)	1.0(2)	0.9(3)	0.6(4)	0.0(4)
	Sn	-0.1(6)	-0.6(5)	-0.2(5)	0.3(5)	0.1(5)
	Bi	0.0(2)	0.05(4)	0.76(7)	0.1(2)	0.30(5)
	Cd	-0.0(2)	0.48(8)	-0.3(1)	0.0(3)	-0.42(8)
BCR step 3	Pb	-0.4(4)	-0.6(3)	-0.2(3)	0.5(4)	0.5(3)
	As	0.4(3)	-0.93(9)	0.6(2)	-0.3(3)	-0.2(2)
	Co	0.5(3)	-1.00(3)	1.00(5)	0.4(4)	-0.9(1)
	Cr	-0.3(2)	-0.95(4)	0.7(2)	-0.8(2)	0.3(1)
	Sn	-0.3(6)	0.6(6)	-0.2(6)	-0.0(6)	-0.0(5)
	Bi	-0.4(2)	-0.47(4)	-0.1(1)	-0.6(2)	0.07(8)
Residue	Cd	-0.5(2)	0.23(4)	-0.69(7)	-0.0(2)	0.56(4)
	Pb	0.6(3)	-0.3(3)	0.8(3)	0.1(5)	-0.5(3)
	As	0.3(5)	-0.9(2)	0.7(4)	-0.4(4)	-0.2(4)
	Co	-1.0(6)	0.7(7)	0.7(7)	-0.9(6)	0.9(6)
	Cr	0.8(1)	-0.64(4)	0.8(1)	0.2(3)	-0.69(3)
	Bi	-0.4(2)	-0.47(5)	0.5(1)	-0.8(2)	0.12(7)
Total BCR + acid attack	Cd	0.2(2)	-0.50(5)	0.65(9)	-0.0(3)	0.22(8)
	Cu	-0.5(3)	-0.5(2)	-0.5(2)	-0.6(3)	-0.1(2)
	Pb	-0.7(2)	-0.57(8)	0.6(2)	-1.0(1)	0.85(9)
	As	0.3(4)	-0.9(2)	0.7(3)	-0.4(4)	-0.2(4)
	Co	0.9(8)	-0.9(8)	-0.9(8)	0.8(9)	-1.0(8)
	Cr	0.8(1)	-0.64(4)	0.8(1)	0.2(3)	-0.68(3)
Total BCR + acid attack	Sn	0.2(6)	-0.2(6)	0.1(6)	-0.2(6)	-0.6(5)
	Bi	-0.5(2)	-0.25(7)	0.0(1)	-0.7(2)	0.06(9)
	Cd	0.0(2)	-0.53(5)	0.5(1)	-0.1(3)	0.42(9)
	Cu	-0.5(3)	-0.5(2)	-0.5(2)	-0.6(3)	-0.0(29)
	Pb	-0.6(2)	-0.7(1)	0.7(2)	-1.0(2)	0.8(1)

The values in parenthesis give the uncertainties (corresponding to the last significant figure) such as, for example, -0.73(7) means  $-0.73 \pm 0.07$ .

values in parenthesis show the uncertainty of the coefficient. It should be pointed out that some cases with high correlation coefficients present uncertainties of the same order as the coefficient that casts doubts on the correlation found. This happened with Co in the first BCR step.

In the first BCR step, the acid-soluble fraction, we found only a high positive correlation between Bi and the percentage in calcium carbonate, the elements presenting a negative correlation (particularly Cr and Sn).

For the second step of the BCR method, the reducible fraction, Co presented a high positive correlation with the clay content in the soil, while Cr appeared strongly correlated with CaCO<sub>3</sub> and pH.

In the third step, the oxidizable fraction, Co showed a negative and highly significant correlation with organic matter and CaCO<sub>3</sub>. Meanwhile, pH showed a certain positive correlation with Co and Pb.

Many remarkable correlations were found in the residue. For example, Cr positively correlated with clay and pH, while Bi and Pb correlated negatively with the fine silt and clay. Also, As and CaCO<sub>3</sub> showed a negative correlation. Since it is in this fraction where the highest percentages of all the elements were found, these results were to be expected on the basis of the low contamination of the soils studied. This has been noted also by other authors, such as López-Sánchez et al. (2002).

For the total concentrations (including the three BCR steps and the acid attacks), we found correlations of Cr with clay and pH, As with CaCO<sub>3</sub> and Pb with fine silt and clay and organic matter.

#### 4. Conclusions

Our results show that the BCR method works reasonably well for Cd, As and Pb only. For these elements



most of the BCR measurements agreed, within the experimental uncertainties to the  $3\sigma$  level, with the reference total concentrations. Therefore, the determination of these elements by sequential extraction appears to be more or less feasible for trace concentrations.

The situation of Co, Cr, Cu and Zn was rather irregular. The agreement between the BCR and the reference methods agreed only in a few horizons for each element. For these elements, the reliability of the sequential extraction for the concentrations considered is quite poor.

Finally, the BCR did not work at all in the case of Ni. It should be emphasized that none of the 10 BCR measurements approached the reference value.

The differences between the Total A and Total B results, as well as the disagreement found between BCR and total analysis, may be due to various factors. One factor may be the protocol of the method, which should be reviewed in some aspects, such as the need for a reference volume for the third step, in which the sample is dried to a “small volume”.

Our findings reflect that the BCR method is not reliable when used for trace concentrations. The BCR method is complex and the possibility of contamination in each step of the procedure can mask the actual element concentrations. Despite this, it could become a valuable tool for identifying the form in which elements are found in soils and for managing them.

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## References

- Aguilar, J., Del Moral, F., Sánchez, J.A., De Haro, S., Fernández, J., Sánchez, S., Marañés, A., Lozano, J., Fernández, E., Rodríguez, T., 2002. Mapa de suelos de Campillos (1022). Servicio de Publicaciones de la Universidad de Almería, Spain.
- Barona, A., Aranguiz, I., Elías, A., 1999. Assessment of metal extraction and contamination in surface soils by 3-step sequential extraction procedure. *Chemosphere* 39, 1911–1922.
- Belzile, N., Lecomte, P., Tessier, A., 1989. Testing readsorption of trace elements during partial chemical extractions of bottom sediments. *Environ. Sci. Technol.* 23, 1015–1020.
- Coetzee, P.P., Guws, K., Pluddermann, S., Yacoby, M., Howell, S., den Drijver, L., 1995. Evaluation of sequential extraction procedures for metal speciation in model sediments. *Water SA* 21, 51–60.
- Davidson, C.M., Thomas, R.P., Mcvey, S.E., Perala, R., Littlejohn, D., Ure, A.M., 1994. Evaluation of a sequential extraction procedure for the speciation of heavy metals in sediments. *Anal. Chim. Acta* 291, 277–286.
- Davidson, C.M., Duncan, A.L., Littlejohn, D., Ure, A.M., Garden, L.M., 1998. A critical evaluation of the three stage BCR sequential extraction procedure to assess the potential mobility and toxicity of heavy metals in industrially-contaminated land. *Anal. Chim. Acta* 363, 45–55.
- Dhoom, R.T., Evans, G.J., 1998. Evaluation of uranium and arsenic retention by soil from a low level radioactive waste management site using sequential extraction. *Appl. Geochem.* 13, 415–420.
- Dorransoro, C., Martín, F., Ortíz, I., García, I., Simón, M., Aguilar, J., Fernández, E., Fernández, J., 2002. Migration of trace elements from pyrite tailing in carbonate soils. *J. Environ. Qual.* 31, 829–835.
- FAO, 1998. World Reference Base for Soil Resources. World Soil Resources Report. 84. ISSS-AISS-IBG. ISRIC.
- Fiedler, H.D., López-Sánchez, J.F., Rubio, R., Rauret, G., Quevauviller, Ph., Ure, A.M., Muntau, H., 1994. Study of the stability of extractable trace metal contents in a river sediment using sequential extraction. *Analyst* 119, 1109–1114.
- Frødesen, A.G., Skjeggstad, O., Tøfte, H., 1979. Probability and statistics in particle physics. Universitetsforlaget, Bergen.
- Gibson, M.J., Farmer, J.G., 1986. Multi-step sequential chemical extraction of heavy metals from urban soils. *Environ. Pollut. Ser. B* 11, 117–135.
- Gómez, J.L., Giráldez, I., Sánchez-Rodas, D., Morales, E., 2000. Comparison of the feasibility of three extraction procedures for trace metal partitioning in sediments from south-west Spain. *Sci. Total Environ.* 246, 271–283.
- Hoffman, E.L., 1992. Instrumental neutron activation in geoanalysis. *J. Geochem. Explor.* 44, 297–319.
- Kabata-Pendias, A., 2001. Trace Elements in Soils and Plants, third ed. CRC Press LLC.
- Kheboian, C., Bauer, C.F., 1987. Accuracy of selective extraction procedures for metal speciation in model aquatic sediments. *Anal. Chem.* 59, 1417–1423.
- López-Sánchez, J.F., Rubio, R., Rauret, G., 1993. Comparison of two sequential extraction procedures for trace metal partitioning in sediments. *Int. J. Environ. Anal. Chem.* 51, 113–121.
- López-Sánchez, J.F., Sahuquillo, G., Rauret, G., Lachica, M., Barahona, E., Gómez, A., Ure, A.M., Muntau, H., Quevauviller, P.H., 2002. Extraction procedures for soil analysis. In: Quevauviller, Ph. (Ed.), *Methodologies for Soil and Sediment Fractionation Studies*, pp. 28–65.
- Mester, Z., Cremisini, C., Ghiara, E., Morabito, R., 1998. Comparison of two sequential extraction for metal fractionation in sediment samples. *Anal. Chim. Acta* 359, 133–142.
- Miller, W.P., Martens, D.C., Zelany, L.W., 1986. Effect of the sequence in extraction of trace metals from soils. *Soil Sci. Soc. Am. J.* 50, 598–601.
- Oughton, D.H., Salbu, B., Riise, G., Lien, H.N., Ostby, G., Noren, A., 1992. Radionuclide mobility and bioavailability in Norwegian and Soviet soils. *Analyst* 117, 481–486.
- Pickering, W.F., 1995. General strategies for speciation. In: Ure, A.M., Davidson, C.M. (Eds.), *Chemical Speciation in the Environment*. Chapman & Hall.
- Press, W.H., Teukolsky, S.A., Vetterling, W.T., Flannery, B.P., 1992. Numerical recipes in Fortran. The Art of Scientific Computing, second ed. Cambridge University Press, New York.
- Rauret, G., Rubio, R., López-Sánchez, J.F., 1989. Optimization of Tessier procedure for metal solid speciation in river-sediments. *Int. Environ. Anal. Chem.* 36, 69–83.
- Sahuquillo, A., López-Sánchez, J.F., Rubio, R., Rauret, G., Thomas, R.P., Davidson, C.M., Ure, A.M., 1999. Use of a certified reference material for extractable trace metals to assess sources of uncertainty in the BCR three-stage sequential extraction procedure. *Anal. Chim. Acta* 382, 317–327.
- Sahuquillo, A., López Sánchez, J.L., Rauret, G., Ure, A.M., Muntau, H., Quevauviller, P.H., 2002. Sequential extraction procedures for sediment analysis. In: Quevauviller, Ph. (Ed.), *Methodologies for Soil and Sediment Fractionation Studies*, pp. 10–27.

- Sheppard, M.I., Stephenson, M., 1997. Critical Evaluation of Selective Extraction Methods for Soils and Sediments, Contaminated Soils. INRA (Les Colleagues, 85), Paris.
- Simón, M., Martín, F., Ortíz, I., García, I., Fernández, J., Fernández, E., Dorronsoro, C., Aguilar, J., 2001. Soil pollution by oxidation of tailing from toxic spill of a pyrite mine. *Sci. Total Environ.* 279, 63–74.
- Szákóvá, J., Tlustos, P., Balík, J., Pavlíková, D., Vanek, V., 1999. The sequential analytical procedure as a tool for evaluation of As, Cd and Zn mobility in soil. *J. Anal. Chem.* 363, 594–595.
- Tessier, A., Campbell, P.G.C., Bisson, M., 1979. Sequential extraction for the speciation of particulate trace metals. *Anal. Chem.* 51, 844–851.
- Thomas, R.P., Ure, A.M., Davidson, C.M., Litteljohn, D., Rauret, G., Rubio, R., López-Sánchez, J.F., 1994. Three-stage sequential extraction procedure for the determination of metals in river sediments. *Anal. Chim. Acta* 286, 423–429.
- Thornton, I., Farago, M., 1997. The geochemistry of arsenic. In: Abernathy, C.O. (Ed.), *Arsenic Exposure and Health Effects*. Chapman & Hall, London.
- Tokalioglu, S., Kartal, S., Elçi, L., 2000. Determination of heavy metals and their speciation in lake sediments by flame atomic absorption spectrometry after a four-stage sequential extraction procedure. *Anal. Chim. Acta* 413, 33–40.
- Ure, A.M., Quevauviller, Ph., Muntau, H., Griepink, B., 1992. B. EUR report. CEC Brussels, 14763, 1992:85.
- Ure, A.M., Quevauviller, Ph., Muntau, H., Griepink, B., 1993. Speciation of heavy metal in soils and sediments. An account of the improvement and harmonisation of extraction techniques undertaken under the auspices of the BCR of the Commission of the European Communities. *Int. J. Environ. Anal. Chem.* 51, 135–151.
- Vangronsveld, J., Cunningham, S.D., 1998. *Metal-contaminated soils: in situ inactivation and phyto restoration*. Springer-Verlag, Berlin, 265 pp.
- Whalley, C., Grant, A., 1994. Assessment of the phase selectivity of the European Community bureau of reference (BCR) sequential extraction procedure for metals in sediment. *Anal. Chim. Acta* 291, 287–295.