

CRM 601, A stable material for its extractable content of heavy metals

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Sequential extraction schemes provide information on the mobility of heavy metals from polluted sediments. The lack of uniformity of these schemes, however, does not allow results to be compared nor the procedures to be validated. In 1987 the Community Bureau of Reference, (BCR, now Standard, Measurements and Testing Programme) of the European Commission launched a programme to harmonise single and sequential extraction schemes for soils and sediments. As a result certified reference material CRM 601 (lake sediment) was prepared and certified for the extractable contents of some trace elements, following a standardised sequential (three-step) extraction procedure. In order to verify the long-term stability of the material an intercomparison exercise was designed with the participation of eight expert laboratories. The results confirm the stability of the 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.

Keywords: *Extractable trace metals; sediments; sequential extraction; quality assurance; certified reference material; stability*

Since the 1970s sequential extraction schemes have been applied by a large number of laboratories to obtain information on the mobility of heavy metals from polluted sediments.^{1–3} The empirical character of this approach has led to proposals of a large number of sequential extraction schemes, all of them based on the same strategy, which is to dissolve, as selectively as possible, the fractions of heavy metal associated with well defined phases. The schemes used a variety of extracting agents, and so the metal distribution patterns produced when different schemes were applied to the same sediment were not comparable. As such there was a need to agree on the procedure that would yield comparable results. In 1987 the Community Bureau of Reference, (BCR, now Standard, Measurements and Testing Programme) of the European Commission launched a programme to harmonise single and sequential extraction schemes for soils and sediments. The development of this programme was discussed at a workshop⁴ organised by BCR in 1992, in which forty representatives of leading laboratories in soil and sediment analysis agreed on a three-steps sequential extraction procedure to study metal partitioning in sediments. The procedure was defined and carefully written and several interlaboratory trials were carried out to validate the method.⁵ Finally a sediment reference material (CRM 601) was prepared and certified for its extractable heavy metals by the validated procedure.⁶ The certification exercise ended in January 1995 and the technical discussion meeting was held in March 1995. Since there was a wide dispersion of the results for some

elements in some fractions some values were stated only as indicative values.

One topic discussed during the certification process was the long-term stability of extractable fractions. When preparing the material the stability of the extractable trace metals was tested for twelve months at several temperatures including 20 and 40 °C. At 40 °C a possible instability of Cu was observed and so the extractable contents of this element were not certified. Since CRM 601 was the first material certified for its extractable metal contents, and no previous experience of this kind of exercise was available, a study on the long-term stability of the material was proposed. Moreover, lyophilised biological material with a moisture content of 3.5%, similar to the CRM 601, could be unstable.⁷ Further removal of moisture may affect the extractability of heavy metals. Thus, in order to confirm the stability of the material an intercomparison exercise was designed with participation of eight expert laboratories, all of which had participated in the previous certification exercise two years ago. Here we describe this interlaboratory study and the results thereof.

Experimental

Description of the sample

The BCR Certified Reference Material 601 is lake sediment collected at several sites in Lake Flumendosa (Italy). The sample pre-treatment, the homogeneity and stability studies, the certification campaign and the certified values are reported elsewhere.³ The CRM samples for the interlaboratory exercise were supplied by the Institute for Reference Materials and Measurements (IRMM, Geel, Belgium), Management of Reference Material Unit, where the CRM 601 is stored at 20 °C. This material can be purchased from the IRMM, and each bottle is accompanied by a certificate and a report describing the work performed.

Intercomparison exercise

Each laboratory that took part in the intercomparison exercise received the following items: four bottles of CRM 601, the BCR three-step protocol for sequential extraction,⁴ the forms for reporting the results and some recommendations to improve their quality control systems. The participants were requested to perform at least five independent determinations for each element (Cd, Cr, Cu, Ni, Pb and Zn) from at least two different bottles of the CRM on different days, and to follow the sequential extraction protocol strictly. The intercomparison exercise ended in October 1997 and the technical discussion meeting was held in December 1997.

Analytical techniques

The techniques used to determine metal concentrations in the extracts were generally FAAS (flame atomic absorption

spectrometry) or ETAAS (electrothermal atomic absorption spectrometry with or without Zeeman background correction). ICP-AES (inductively coupled plasma atomic emission spectrometry) was also used by some laboratories.

Technical discussion

The sources of error and the precautions taken to overcome them were discussed at the technical meeting. The participating laboratories applied their determination methods only when the method was under control, *i.e.*, the standard deviations observed in the laboratory were in accordance with the normal practice of the laboratories. Most of the errors detected were due to the calibration rather than to the application of the extraction procedure. It was recommended that the participants should use pure metal solutions (Cd, Cu, Ni, Pb and Zn or NIST certified $K_2Cr_2O_7$) as calibrants. If these standards were not available, the two standard solutions of different origin were to be used, and their concentration was to be checked periodically. The participants agreed that the data obtained in this exercise might be useful to the people purchasing the material and agreed to advise the Scientific Evaluation Group for the Certification of Reference Materials of the Standards, Measurement and Testing Programme to include such data as an appendix to the certification report.

Results and discussion

The sets of results found acceptable on technical and statistical grounds were presented in the form of bar-graphs. Some examples of the results obtained are given in Figs. 1–5. In the bar-graphs, the length of a bar corresponds to the 95% confidence interval of the mean of laboratory means. The interlaboratory means were calculated as the arithmetic mean of laboratory means. This value and the certified value are featured as a vertical dotted line and a solid vertical line, respectively; the uncertainty on mean values is given by the half width of the 95% confidence interval of the mean of laboratory means.

The results and the certified values and their uncertainties (half width of the 95% confidence intervals) are given in Table

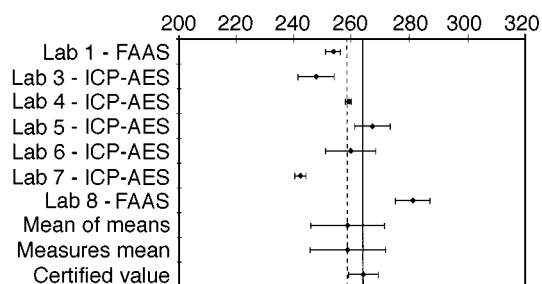


Fig. 1 Bar-graph for extracted zinc in the first step. The plotted values and their uncertainties (half width of the 95% confidence intervals) are as mass fractions, in $mg\ kg^{-1}$, of the respective extracts.

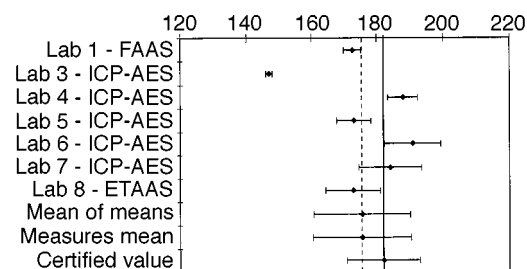


Fig. 2 Bar-graph for extracted zinc in the second step. The plotted values and their uncertainties (half width of the 95% confidence intervals) are as mass fractions, in $mg\ kg^{-1}$, of the respective extracts.

1 as mass fractions of the respective extracts obtained at the first, second and third steps (based on dry mass) in $mg\ kg^{-1}$. For an easy comparison of the data the table also includes the percentage of recovery as well as the associated uncertainty obtained.

The results for the first step compare well with the certified values for Cd, Cr, Ni and Zn showing recoveries ranging from 98 to 108%. For Pb the amount extracted is lower (77% recovery) but the two confidence intervals overlap due to the widerange of data. For Cu the amount extracted is significantly higher (125% recovery) than the indicative value. This element was not certified because of the suspicion of long-term instability inferred from the stability data at 40 °C, probably due to small changes in Mn oxides and organic matter phases of the sediment.

In the second step the recoveries range from 92 to 113%. Cr and Zn presented good agreement with the certified/indicative values. For Cd, Ni and Pb larger standard deviations were observed, but they were also in agreement with the certified/indicative values. For Cu the amount extracted is higher but the wide range of the results obtained made it difficult to draw conclusions. From examination of the raw data, two laboratories seem to be responsible for the high standard deviation. Both laboratories attributed this to the higher pH values of their final extracts, which produced a lower extraction of the metal in the solution and consequently lower amounts of metal were detected.

For the third step, the amounts extracted for Cd, Cr, Cu, Pb and Zn compare well with the certified/indicative values obtaining recoveries ranging from 91 to 106%. For these elements the uncertainties were of similar magnitude to those obtained in the certification exercise. For Ni a lower recovery is obtained (79%), but the wide dispersion of data makes it difficult to draw conclusions.

Conclusions

The results of the study confirm the stability of the extractable contents of Cd, Cr, Ni, Pb and Zn in this type of material, and

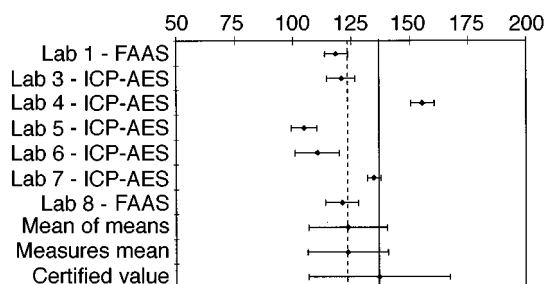


Fig. 3 Bar-graph for extracted zinc in the third step. The plotted values and their uncertainties (half width of the 95% confidence intervals) are as mass fractions, in $mg\ kg^{-1}$, of the respective extracts.

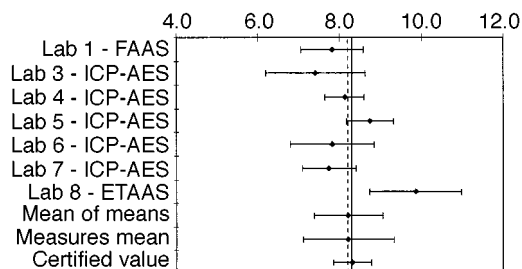


Fig. 4 Bar-graph for extracted nickel in the first step. The plotted values and their uncertainties (half width of the 95% confidence intervals) are as mass fractions, in $mg\ kg^{-1}$, of the respective extracts.

Table 1 Results obtained in the interlaboratory study on long-term stability of the extractable metal contents in CRM 601

	Certified value/ mg kg ⁻¹	Uncertainty/ mg kg ⁻¹	<i>p</i> *	Long-term value/ mg kg ⁻¹	Uncertainty/ mg kg ⁻¹	<i>p</i> *	Recovery (%)	Recovery uncertainty (%)
First step								
Cd	4.14	0.23	11	4.46	0.63	7	108	14
Cr	0.36	0.04	12	0.37	0.087	6	103	24
Cu	8.32 [†]	0.46	9	10.4	0.43	6	125	3
Ni	8.01	0.73	10	8.22	0.83	7	103	10
Pb	2.68	0.35	11	2.07	0.49	7	77	24
Zn	264	5.0	12	259	13	7	98	5
Second step								
Cd	3.08	0.17	10	3.05	0.96	6	99	31
Cr	1.43 [†]	1.0	13	1.42	0.83	7	99	58
Cu	5.69 [†]	3.2	10	6.37	3.56	6	112	56
Ni	6.05	1.1	11	5.55	1.5	7	92	27
Pb	33.1	10	9	37.3	19	7	113	51
Zn	182	11	12	175	15	7	96	9
Third step								
Cd	1.83	0.20	11	1.80	0.17	5	98	9
Cr	18.3 [†]	4.47	14	19.4	0.91	6	106	5
Cu	116 [†]	26	15	116 [†]	9.0	7	100	8
Ni	8.55	1.04	9	6.75	0.86	7	79	13
Pb	109	13	12	108	19	7	99	18
Zn	137 [†]	30	14	124	17	7	91	7

* *p* = number of data sets. † Values obtained in the certification campaign, but finally not certified.

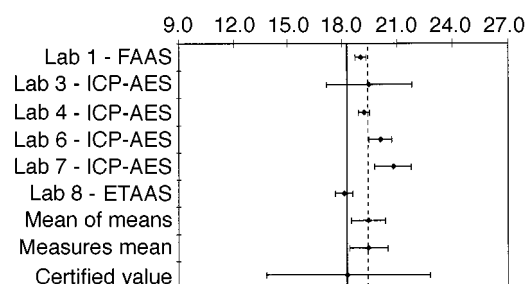


Fig. 5 Bar-graph for extracted chromium in the third step. The plotted values and their uncertainties (half width of the 95% confidence intervals) are as mass fractions, in mg kg⁻¹, of the respective extracts.

demonstrate that the preparation of CRMs for extractable trace metal contents in similar matrices can be achieved.

The following laboratories participated in the intercomparison on long-term stability of CRM 601: Agricultural Research Centre, Institute of Soils and Environment (Jokioinen, Finland); Bund. für Materialforschung und Prüfung (Berlin, Germany); Department of Analytical Chemistry, University of Barcelona, (Barcelona, Spain); Department of Pure and Applied Chemistry, University of Strathclyde (Glasgow, United Kingdom); Environment Institute, Joint Research Centre (Ispra, Italy); Estación experimental del Zaidin, CSIC (Granada, Spain);

Institut National de Recherche Agronomique (Villeneuve d'Ornon, France); The Macaulay Land Use Research Institute (Aberdeen, United Kingdom). J.F.L.-S., A.S., R.R. and G.R. also thank CEC, DGICYT and CIRIT for the financial support of this work.

References

- Salomons, W., and Förstner, U., *Environ. Technol. Lett.*, 1980, **51**, 506.
- Pickering, W. F., *Ore Geol. Rev.*, 1986, **1**, 83.
- Kersten, M., and Förstner, U., *Trace Element Speciation: Analytical Methods and Problems*, ed. Batley, G. E., CRC Press, Boca Raton, FL, 1989, ch. 8.
- Proceedings of the Workshop on the Sequential Extraction of trace metals in soils and sediments*, ed. Albaigés, J., Rauret, G., and Quevauviller, Ph., *Int. J. Environ. Anal. Chem.*, 1993, **51**.
- Quevauviller, Ph., Rauret, G., Muntau, H., Ure, A. M., Rubio, R., López-Sánchez, J. F., Fiedeler, H. D., and Griepink, B., *Fresenius' J. Anal. Chem.*, 1994, **349**, 808.
- Quevauviller, Ph., Rauret, G., López-Sánchez, J. F., Rubio, R., Ure, A. M., and Muntau, H., *Sci. Total Environ.*, 1997, **205**, 223.
- Pauwels, J., personal communication.

Paper 8/02720J
Received April 9, 1998
Accepted May 21, 1998