

# Certified reference material (CRM 414) for the quality control of trace element analysis in plankton

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**Summary.** Analyses of plankton are performed by a number of organisations to investigate the transfer and uptake of toxic elements along the trophic chain and to monitor the levels of contamination of different aquatic environments. In order to obtain reliable transfer functions in environmental models or to use plankton as an indicator organism for the assessment of environmental pollution, these analyses should give accurate results. As accuracy requires quality control and the application of certified reference materials (CRMs), a certification campaign has been conducted by the Community Bureau of Reference (BCR). A plankton material was collected in a freshwater pond, lyophilised, homogenised and bottled and its homogeneity and long-term stability were verified. The material (CRM 414) was analysed by a group of 15 selected laboratories having given proof of their adequate QC and using different analytical methods. The contents of As, Cd, Cr, Cu, Hg, Mn, Ni, Pb, Se, V and Zn are certified. This paper presents the certification work performed.

## Introduction

Analyses of phyto- and zooplankton are important to investigate the transfer and uptake of toxic elements along the trophic chain, to define the role of these organisms in the biogeochemical pathways. Furthermore, plankton may be used as an indicator for water pollution and to compare the levels of contamination of different aquatic environments. The determination of trace elements is still troublesome as shown in an intercomparison between 18 laboratories on trace elements in plankton [1], where the presence of systematic errors was demonstrated. The quality of analysis of plankton material may not be controlled by using other marine CRMs already existing for the purpose of monitoring the aquatic environment due to its composite nature (mixture of sedimentary and biogenic particles). The Community Bureau of Reference (BCR) of the Commission of the European Communities has therefore been invited to procedure a plankton material. This material (CRM 414) was prepared in 1989 and has been certified for trace elements of most interest, i.e. As, Cd, Cr, Cu, Fe, Hg, Ni, Mn, Pb,

Se, V and Zn; it completes a series of existing CRMs for the quality control of analyses in the aquatic environment (e.g. lake and river sediments CRMs 280 and 320 [2], aquatic plants CRMs 060 and 061 [3] and freshwater materials CRMs 398 and 399 [4]).

## Certification procedure

The only possibility for any laboratory to ensure accuracy and to compare its results with those of others in a simple manner is to verify the analytical procedure by means of a so-called matrix reference material certified in a reliable manner. The laboratory which measures such a certified reference material (CRM) by its own procedure and finds a value in disagreement with the certified value is thus warned that its measurement includes an error, the source of which must be identified [5].

A series of steps was undertaken in order to ensure that no substantial systematic errors were left undetected in the certification of the material presented in this paper, in particular:

- (i) special care to avoid contamination, losses, incomplete digestion, manipulation errors, etc.;
- (ii) application of good QC-principles, e.g. control of calibration, detection and removal of interferences, peak overlap, background corrections, and laboratories well under control (e.g. performance, experience, clean areas, training and motivation of staff, application of QA system etc.);
- (iii) comparison of different methods applied in different laboratories for the detection of sources of error inherent to one particular technique or to the laboratory itself.

## Participating laboratories

The material was collected by the CNR Institute for Limnology (Pallanza, I) and prepared by the CEC Joint Research Centre of Ispra (I) whereas the homogeneity and stability studies were carried out at Forschungszentrum für Umwelt und Gesundheit in Neuherberg (D) and at the Netherlands Energy Research Foundation in Petten (NL), respectively. A characterisation of the material at the level of the particles was performed at Universitaire Instellingen Antwerpen in Wilrijk (B).

The analyses were performed by the following laboratories:

- Aristotelian University, Laboratory of Analytical Chemistry, Thessaloniki (GR)
- Danish Isotope Centre, Copenhagen (DK)
- ECN Energieonderzoekcentrum Nederland, Petten (NL)
- Forschungszentrum für Umwelt und Gesundheit, Neuherberg (D)
- Istituto Superiore di Sanità, Roma (I)
- Instituut voor Nucleaire Wetenschappen, Rijksuniversiteit Gent (B)
- Kernforschungsanlage Jülich (D)
- Labor für Spurenanalytik, Bonn (D)
- National Food Administration, Uppsala (S)
- NLR “Demokritos”, Agia Paraskai Attikis (GR)
- Presidio Multizonale di Prevenzione, Sezione Chimica, Venezia (I)
- RISOE National Laboratory, Roskilde (DK)
- Universidad Complutense, Facultad de Química, Madrid (E)
- Universitaire Instelling Antwerpen, Department of Chemistry, Wilrijk (B)
- Università di Pavia, Chimica Generale, Pavia (I)

### Preparation

The plankton was collected in April and May 1988 from several ponds situated in the vicinity of the river Po. The ponds were fed by the Po water downstream a power plant. The relatively high water temperature accelerated plankton growth allowing the collection of the total amount necessary for the reference material within a relatively short period. The collection was done with a manually-operated net with 125 µm apertures. The wet material collected was packed in double-layer polythene bags and was kept at –20°C until freeze-drying.

When sufficient wet material was collected, it was freeze-dried, ground in a zirconia ball mill and sieved to pass 125 µm apertures. The resulting powder was collected in a mixing drum and homogenised by continuous rotation under dry Ar over two weeks. Cleaned brown glass bottles were filled with approximately 5 g of material and closed with screw caps and plastic inserts. A PTFE-ball was added to facilitate later re-homogenisation in case segregation would occur.

### Particle characterisation

A microscopical examination of the fresh material showed that the large majority of the organisms (> 98%) were cladocerans mainly of the species *Daphnia magna* with the occasional presence of a few copepods and rotifers.

Individual particles of the material were analysed by automated electron microprobe analysis which allows to detect elements with higher atomic number (e.g. from Al). Several morphological types as well as chemical classes were observed which could be summarized in 5 major particle types according to the most abundant element or elements: Si-rich particles, Ca-rich particles, Ca-P rich particles, clay minerals (Al-Si-K-Fe) and organic particles (mostly S and P). The automated analysis was repeated for four indepen-

**Table 1.** Results of classification (mean values of 4 replicate particle countings and standard deviation) in % of total number of particles

Si-rich	Ca-rich	Ca-P-rich	“Clay”	“Organic”
14.9 ± 1.4	1.9 ± 1.5	1.4 ± 0.9	33.4 ± 1.9	1.3 ± 0.5

**Table 2.** Preliminary homogeneity study on C, H and N

Element	CV % within-bottle <sup>a</sup>	CV % between-bottle <sup>b</sup>
C	0.95	1.07
H	1.51	1.57
N	1.49	1.02

<sup>a</sup> 10 replicate determinations in one bottle

<sup>b</sup> 1 determination in each of 14 bottles

dently prepared samples. The classification is based on the number of particles associated to corresponding chemical elements.

The results are listed in Table 1. The high standard deviations observed account for the combination of errors on sampling, analysis and classification. It could be concluded that the percentage of “inorganic” particles (which are mostly of the clay-type) is approximately 50%. Expressed on a mass basis the inorganic fraction should be higher since the density of the inorganic particles is higher.

In order to evaluate the proportion of organic material, and therefore the amount of mineral material, the ash content of the material was determined in duplicate by heating 1 g of material at 750°C until a constant mass was attained. The loss of mass was 18.45%.

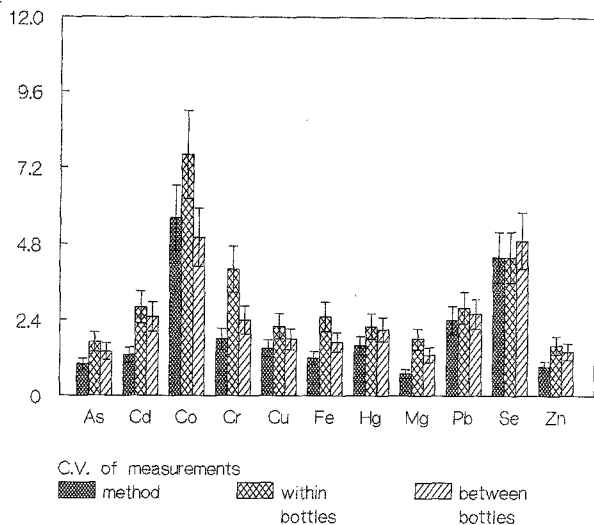
### Homogeneity study

#### Preliminary study

Preliminary tests to assess the within- and between-bottle homogeneity were performed on major elements (C, N and H) in order to obtain a first estimate on the suitability of the material as a CRM. Analyses were performed on intakes of 0.5 to 2 mg with a C-H-N elemental analyser. The within-bottle homogeneity was assessed by 10 replicate determinations on the rehomogenised content of one bottle whereas the between-bottle homogeneity was verified on intakes taken from 14 bottles set aside at regular intervals during the whole period of bottling. The obtained coefficients of variation (CVs) are presented in Table 2. Statistical tests (ANOVA) applied to the whole set of data did not allow to detect any inhomogeneity.

#### Homogeneity study of trace element contents

The between bottle homogeneity after rehomogenisation of the bottle contents was verified by the determination of As, Cd, Co, Cr, Cu, Fe, Hg, Mg, Pb, Se and Zn on intakes of 50, 100 and 250 mg taken from 15 bottles set aside at regular intervals during the whole period of bottling. The within bottle homogeneity was assessed by 15 replicate determinations on the rehomogenised content of one bottle. Each bottle containing a PTFE ball was manually shaken for



**Fig. 1.** Results of the homogeneity study for As, Cd, Co, Cr, Cu, Fe, Hg, Mg, Pb, Se at Zn at the 100 mg level of intake. The length of the bar on each block represents  $2 U_{CV}$

5 min to eliminate segregations which might have occurred during transport and storage.

Analyses were performed by CVAAS (Hg), HAAS (As and Se), ETAAS (Cd and Pb) and ICP (Co, Cr, Cu, Fe, Mg and Zn) after pressurised digestion with nitric acid in a quartz vessel at  $170^{\circ}\text{C}$  for ca. 8 h. The CV of the final method of determination was obtained by 15 replicate measurements on one digest solution (1.5 g taken resulting in 100 ml).

The CVs for the elements are summarised in Fig. 1. An F-test at a significance level of 0.01 did not reveal significant differences between the within- and between-bottle variances. In most cases, no significant differences were observed between the CV of the method and the CV within- or between-bottles as the overlap was within the total uncertainty  $U_T$  of the CV (an approximation of the uncertainty  $U_{CV}$  of the CV is calculated as follows:  $U_{CV} \approx CV/\sqrt{2n}$ ).

No inhomogeneities being detected within a given method, the material is considered to be homogeneous at a level of 50 mg and above.

#### Simulation of segregation during transport

Additional tests were performed to assess possible segregation effects upon transport. Plankton material was loaded in a plastic tube which was mounted vertically and gently vibrated at a 50 Hz frequency for 100 h; the tube was then cut in three sections, i.e. bottom, middle and top. The study of possible segregation was done on the basis of the variations of the particle distribution as described in the section on particle characterisation. This principle was chosen for two main reasons:

- differences of composition between the three layers are reflected in the size distribution;
- size distributions are representative of the total particle population.

The results (Table 3) indicate that the particle sizes are decreasing towards the bottom of the tube after vibration. The three distributions were submitted to a Kolmogorov

**Table 3.** Simulation of transport effects (segregation tests) and homogeneity tests on the particle size distribution (on rehomogenised content of 1 bottle)

	Segregation tests Mean ( $\mu\text{m}$ )	Homogeneity test	
		Mean ( $\mu\text{m}$ )	SD
Top	3.889	2.894	0.003
Middle	2.958		
Bottom	2.625		

distribution test and were found to be statistically different from each other at a 0.05 significance level. This clearly demonstrates that segregation may occur upon transport.

In addition, the sample homogeneity with regard to particle size distribution was again verified by shaking manually three different samples for 5 min after vibration (glass container with the PTFE ball) and by sizing 5000 particles in each of the three samples. The Kolmogorov distribution test did not reveal any statistical differences in the results obtained at the 0.05 significance level. The mean value obtained is given in Table 3 along with the standard deviation.

This study highlights the need to carefully shake the samples prior to analysis as segregation may occur during transport of the material. The homogeneity of the particle size distribution is found to be good after shaking.

#### Stability study

The stability of the trace metal content was tested to determine the suitability of the plankton material as a reference material. Bottles were kept at, respectively,  $-20^{\circ}\text{C}$ ,  $+20^{\circ}\text{C}$  and  $40^{\circ}\text{C}$  over a period of 12 months, and minor (Na) and trace elements (As, Br, Co, Cr, Fe, Mn, Se and Zn) were determined at regular intervals during the storage period. Tests were made at the beginning of the storage period and after 3, 6 and 12 months. Analyses were performed by INAA using irradiation with thermal neutrons of both a 100 kW and a 50 MW research reactor.

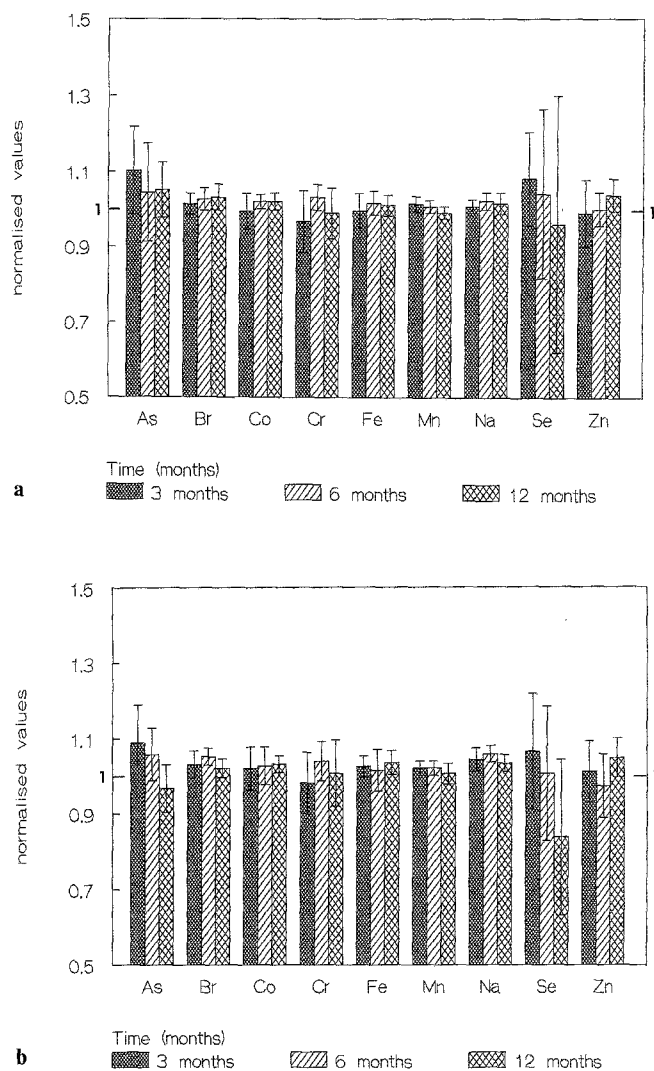
Any change of results on element composition in time indicates an instability provided that a good long-term analytical reproducibility is obtained. At  $-20^{\circ}\text{C}$  changes of any kind proceed slowly, whereas at  $+40^{\circ}\text{C}$  instability is more likely. Instability can therefore also be detected by comparing the contents of different elements in samples stored at different temperatures at the various occasions of analysis. Assuming that samples stored at  $-20^{\circ}\text{C}$  in the dark are stable, they can serve as reference for the samples stored at  $+20^{\circ}\text{C}$  and  $+40^{\circ}\text{C}$ .

The stability assessment was based on the calculation of the ratio ( $R_T$ ) of the mean values ( $\bar{X}_T$ ) of the 5 measurements made at  $+20^{\circ}\text{C}$  and  $+40^{\circ}\text{C}$  versus the mean value ( $\bar{X}_{-20^{\circ}\text{C}}$ ), from 5 determinations made at the same occasion of analysis on samples stored at a temperature of  $-20^{\circ}\text{C}$ :

$$R_T = \bar{X}_T / \bar{X}_{-20^{\circ}\text{C}}$$

The uncertainty  $U_T$  has been obtained from the coefficient of variation (CV) of 5 measurements obtained at each temperature:

$$U_T = (CV_T^2 + CV_{-20^{\circ}\text{C}}^2)^{1/2} \cdot R_T / 100$$



**Fig. 2.** **a** Results of the stability study after 3, 6 and 12 months at +20°C for As, Br, Co, Cr, Fe, Mn, Na, Se and Zn. The length of the vertical bar on each block represents  $2 U_T$ . **b** Results of the stability study after 3, 6 and 12 months at +40°C for As, Br, Co, Cr, Fe, Mn, Na, Se and Zn. The length of the vertical bar on each block represents  $2 U_T$ .

The methodological CV of INAA was obtained from counting statistics only; variations resulting from other experimental parameters such as irregular loading of the vial, counting geometry etc. are evaluated in the residual CV analysis, which is considered to describe inhomogeneity but therefore gives a pessimistic estimate of it.

Figure 2a and 2b show the ratios of the mean values ( $R_T$ ) and the uncertainty ( $U_T$ ). In the case of ideal stability,  $R_T$  should be 1. In practice however, there are some random variations due to the uncertainty of the measurement.

On the basis of the results, it was concluded that no instability could be demonstrated. The material will be monitored further at regular intervals.

### Techniques used for certification

15 laboratories from 8 European countries participated in the certification (see section analyses). All proved that they

**Table 4.** Summary of techniques of final determination

Element	Techniques
As	HAAS, HICP, ICPMS, RNAA, SPEC, ZETAAS
Cd	DPASV, ICPMS, IDMS, MS, ZETAAS
Cr	DPASV, INAA, ETAAS, ICPAES, RNAA, ZETAAS
Cu	DPASV, FAAS, ICPAES, ICPMS, MS, RNAA, ZETAAS
Hg	CVAAS, HICP, RNAA
Mn	ETAAS, FAAS, INAA, ICPMS
Ni	CSV, DPASV, ETAAS, ICPAES, INAA, ZETAAS
Pb	DPASV, ETAAS, ICPMS, IDMS, ZETAAS
Se	DPCSV, MS, HAAS, HICP, INAA, ZETAAS
V	DPASV, ICPAES, INAA, ZETAAS
Zn	DPASV, FAAS, ICPAES, ICPMS, IDMS, INAA, MS

CSV = Cathodic stripping voltammetry; CVAAS = Cold vapour atomic absorption spectrometry; DPASV = Differential pulse anodic stripping voltammetry; DPCSV = Differential pulse cathodic stripping voltammetry; ETAAS = Electrothermal atomic absorption spectrometry; FAAS = Flame atomic absorption spectrometry; HAAS = Hydride formation atomic absorption spectrometry; HICP = Hydride formation inductively coupled plasma atomic emission spectrometry; ICPAES = Inductively coupled plasma atomic emission spectrometry; ICPMS = Inductively coupled plasma mass spectrometry; INAA = Instrumental neutron activation analysis; MS = Mass spectrometry; RNAA = Neutron activation analysis with radiochemical separation; SPEC = U.V. or visible light spectrometry; ZETAAS = ETAAS with Zeeman background correction

were working under a good quality control system. Table 4 summarizes the different techniques of final determination for the different elements as used by these laboratories.

The pretreatment techniques were digestion with combination of acids in a pressurised or atmospheric mode, programmed dry ashing, combustion and irradiation with thermal neutrons. A detailed description of these methods is given in the certification report [6].

### Technical evaluation of the results

Due to the presence of clay particles, risks of incomplete mineralisation were likely; therefore, the participants were requested to indicate whether they had used HF for the digestion of the plankton material or could prove that the total element content had been measured (e.g. by checking the residue).

The deuterium background correction was not recommended for the AAS determination of Cr in this material since the intensity of the lamp is already very low at the wavelength used (276 nm).

The accepted results and methods were discussed amongst all participants in a technical meeting and various statistical tests were applied thereafter which are described in the certification report [6]. The certified values (based on dry mass) are presented in Table 5 along with their calculated uncertainties.

### Comparison of the methods

In the certification exercise of some elements three or more laboratories applied the same technique of final determi-

**Table 5.** Certified contents (in µg/g on a dry matter basis) of As, Cd, Cr, Cu, Hg, Mn, Ni, Pb, Se, V and Zn in CRM 414

	Certified value	Uncertainty
As	6.82	0.28
Cd	0.383	0.014
Cr	23.8	1.2
Cu	29.5	1.3
Hg	0.276	0.018
Mn	299	12
Ni	18.8	0.8
Pb	3.97	0.19
Se	1.75	0.10
V	8.10	0.18
Zn	112	3

nation. In such a case it was possible to compare the results per technique. A grand mean of the means of all the three or more laboratories applying the same technique of final determination was calculated. The obtained grand means were then compared to investigate whether a particular bias would be attributed to any method. Table 6 presents the results of the evaluation for Cu and Pb. This evaluation was not possible for the other elements as the number of similar techniques was not sufficient to allow a comparison of the methods.

As shown in the table, the CVs within one method are systematically larger than those between different techniques. Consequently, it cannot be inferred that results of one technique do not agree with those of other techniques as verified for Cu and Pb.

#### Indicative values

During the course of the certification some laboratories individually determined other elements. These results (mean values) are given in the Table 7 together with the standard deviation obtained, the method used and the number of sets of results. Other elements were determined by a single laboratory and the data are given for information (mean of 5 replicates) together with the standard deviation obtained and the method used.

It is emphasized that these values are not certified.

#### Precautions for use of this CRMs

For this plankton material having relatively low contents of heavy metals, care must be taken to avoid contamination, i.e. care must be paid to obtain reagents of sufficient purity and the work must be carried out in an atmosphere which meets standard requirements of clean work.

In the preparation step of the material all care was applied to achieve a good between bottle homogeneity, i.e. the composition with respect to the certified elements in the bulk of all bottles is the same. Upon transport, the material in the bottle will segregate. Therefore the contents of each bottle must be rehomogenised before taking a subsample from the bottle. If this is not done properly, the CVs will be larger and errors may occur.

Manual shaking for 5 min or mechanical shaking, combining a rolling and a tumbling movement, is sufficient.

**Table 6.** Results of the evaluation of the consistency of the methods applied for Cu and Pb

Element	Techn. of final determination	CV % between means of lab. with the same technique	NR of sets of results	CV % between means of diff. techniques
Cu	FAAS	3.99	3	5.83
	RNAA	2.80	3	
	DPASV	10.69	3	
Pb	ZETAAS	4.69	3	3.41
	DPASV	8.26	3	

**Table 7.** Indicative values in CRM 414

Element	Mean	S.D.	P	Techniques used
Co (µg/g)	1.43	0.06	4	INAA, ICP, CSV
K (µg/g)	7.55	0.17	2	INAA
Fe (µg/g)	1.85	0.19	3	INAA, ICP
Mo (µg/g)	1.35	0.20	2	INAA, ICP
Sc (µg/g)	0.54	0.02	2	INAA
Sr (µg/g)	261	25	2	INAA, ICPMS
Al (mg/g)	1.80	0.03	1	ICPAES
Ba (µg/g)	31	2	1	ICPAES
Br (µg/g)	55	1	1	INAA
C (mg/g)	90	1	1	Comb. Cath.
Ca (mg/g)	65	2	1	ICPAES
Cs (µg/g)	0.41	0.02	1	INAA
La (µg/g)	1.3	0.2	1	INAA
Mg (mg/g)	2.4	0.08	1	ICPAES
N (mg/g)	409	2	1	ICPAES
Na (mg/g)	8.3	0.4	1	ICPAES
P (mg/g)	12.3	0.6	1	ICPAES
Rb (µg/g)	11.6	0.2	1	ICPMS
S (mg/g)	6.8	0.2	1	ICPAES
Sn (µg/g)	1.18	0.12	1	ICPAES
Sb (µg/g)	0.086	0.010	1	INAA
Tl (µg/g)	0.047	0.002	1	MS
Ti (mg/g)	48	5	1	ICPAES
U (µg/g)	0.30	0.06	1	INAA

p: sets of results (each of 5 replicates)

The correction to dry mass should be made by taking a separate portion of 100 mg and drying in an oven at 102°C for 3–4 h (successive weighings should not differ by more than 0.2 mg).

Care must be taken that the whole analytical sample is digested. This material is a mixture of mineral and organic particles; trace metals such as Cd, Cu and Cr are likely to be bound to silicate and to clay particles. Therefore, pressurised digestion with oxidising acids, followed by repeated additions of hydrofluoric/nitric acid and evaporation to dryness are recommended.

The effects of HF-treatment have been investigated for Cd, Cr, Cu, Mn, Pb and Zn: no major difference (within the uncertainty of the method) between the digestion with or without HF was observed for Mn and Zn. After HF treatment however, contents of Cu and Pb were significantly higher (respectively 6.4 and 9.6%) whereas Cd and Cr contents considerably increased by respectively 27% and 26%.

**Table 8.** Programmes used for the study of micro-wave digestion

Programme I			Programme II		
Reagents	Time (min)	Power (W)	Reagents	Time (min)	Power (W)
10 ml HNO <sub>3</sub>	5	10	7 ml HCl + 3 ml HNO <sub>3</sub>	5	40
	10	30			
	10	60			
10 ml HNO <sub>3</sub> 2 ml H <sub>2</sub> O <sub>2</sub> 5 ml H <sub>2</sub> O	10	60	3 ml HNO <sub>3</sub> 3 ml HNO <sub>3</sub> 1 ml H <sub>2</sub> O <sub>2</sub> 5 ml H <sub>2</sub> O	10	50
	5	60			
	5	50			

**Table 9.** Results of the micro-wave digestion study for some elements

Elements	Programme I		Programme II		Certified values
	ICPMS	ICP	ICPMS	ICP	
Cd	0.376 ± 0.068		0.374 ± 0.003		0.383 ± 0.014
Cu	32.12 ± 5.8	31.08 ± 0.73		30.03 ± 0.5	29.5 ± 1.3
Mn	223 ± 34	281 ± 19		267 ± 11	299 ± 12
Pb	3.73 ± 0.38				3.97 ± 0.19
Zn	112 ± 3	114 ± 2	108 ± 9	112 ± 4	112 ± 3

All the values are expressed in µg/g

In addition, an independent study to investigate the suitability of micro-wave digestion for this material has been performed by the CNRS (Service Central d'Analyse, Vernaison, F). An open system was used and two programmes were tested which are described in Table 8; the results (Table 9) allowed to conclude that the open micro-wave digestion techniques described were suitable for the determination of Cd, Cu, Mn, Pb and Zn in this material [7]. A complete mineralisation could be achieved with the addition of H<sub>2</sub>O<sub>2</sub> as demonstrated with the analysis of other CRMs (e.g. estuarine sediment CRM 277).

#### Availability

The reference materials are available from the BCR, Commission of the European Communities, Rue de la Loi 200, B-1049 Brussels (Fax: +32-2.2958072). Each bottle is accompanied by a certificate and a report describing the work performed (preparation, homogeneity and stability studies, analytical methods used and individual results).

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