



The additional certification of the Pb mass fraction in sediment material BCR-320R (channel sediment)

T. Venelinov, A. Held



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BCR information
REFERENCE MATERIALS

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fraction in sediment material
(channel sediment)**

BCR-320R

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Disclaimer

Certain commercial equipment, instruments, and materials are identified in this report to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the European Commission, nor does it imply that the material or equipment is necessarily the best available for the purpose.

Abstract

This report describes the additional certification of Pb in the sediment reference material BCR-320R.

| Material | Number of valid data sets | Certified value [mg/kg] | U_{CRM} [mg/kg], $k = 2$ |
|----------|---------------------------|----------------------------|-------------------------------|
| BCR-320R | 6 | 85 | 5 |

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Glossary

| | |
|----------------------|---|
| AAS | Atomic Absorption Spectrometry |
| BCR | Community Bureau of Reference |
| CRM | Certified Reference Material |
| DPASV | Differential Pulse Anodic Stripping Voltammetry |
| ETAAS | Electrothermal AAS |
| FAAS | Flame AAS |
| ICP-AES | Inductively Coupled Plasma Atomic Emission Spectrometry |
| ICP-MS (Q / HR / MC) | Inductively Coupled Plasma Mass Spectrometry (Quadrupole / High Resolution i.e. Sector Field / Multicollector Instrument) |
| ID | Isotope Dilution Technique |
| ID-TIMS | Thermal Ionization Mass Spectrometry using the Isotope Dilution technique |
| k'_2 | Factor for the two-sided 95 % tolerance limits for a normal distribution |
| M | Minimum sample mass |
| m | Average mass used during the measurements |
| MSB | Mean Square between bottles |
| MSW | Mean Square within bottles |
| RSD | Relative Standard Deviation |
| S_{bb} | Relative between-unit variability |
| S_{wb} | Standard deviation within bottle |
| S_m | Relative standard deviation of the homogeneity experiment |
| S_{meas} | Relative measurement variability |
| SI | Système International d'unités (international system of units) |
| u_{bb} | Relative standard uncertainty related to a possible between-bottle heterogeneity |
| u_{bb}^* | Relative heterogeneity that could be hidden by method repeatability |
| u_c | Relative combined uncertainty of the certified value |
| $u_{c,bb}$ | Relative combined uncertainty of the between-unit measurement |
| u_{char} | Standard uncertainty of the characterisation |
| U_{CRM} | Expanded uncertainty of a certified value |
| u_{lts} | Relative standard uncertainty of stability |
| u_{target} | Maximum relative uncertainty for sampling |
| t | Proposed shelf life in a stability study |
| \bar{t} | Average of all time points in a stability study |
| t_i | Time point for each replicate in a stability study |

1. Introduction

Accurate data from the analysis of sediments are required for a number of purposes. First of all, sediments are in a constant exchange with the water column above. They actively contribute to the removal or uptake of pollutants from the water. Due to their subsequent deposition, sediments can also provide a historic record of water quality or pollution in their depth profile. Monitoring of water quality (and thus the closely related sediments) has gained increasing importance over the last years, in particular with the publication of the Water Framework Directive [1]. For monitoring activities, also the comparability of data obtained in different parts of Europe is important. CRMs are an essential tool in improving comparability. Also dredged sediments have to be disposed appropriately. Consequently, the quality of analytical data can have financial and ecological impacts.

This report describes the additional certification of Pb in BCR-320R (channel sediment). This material has already been certified for its total trace element content (As, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Sc, Th, Tl, U, V and Zn). Indicative values have been established for Se and Sn. Difficulties with the characterisation of Pb made an additional certification necessary. During the first characterisation exercise in 2002, a result for Pb obtained by one of the participating laboratories significantly differed from the rest, but no reasons were found to reject the result obtained. Therefore a decision was taken to use completely different laboratories for the present characterisation.

2. Participants

Characterisation 2002 (used for long-term stability)

| Participant | Activity |
|--|----------|
| European Commission, JRC, Institute for Reference Materials and Measurements (EC-JRC-IRMM), Geel, BE | H, S |
| Nederlands Meetinstituut (NMI), Afdeling Chemie, Delft, NL | S |
| Nuclear Research and Consultancy Group, Petten, NL | S |

Characterisation 2007

| Participant | Activity |
|---|----------|
| ALS Laboratory Group, Praha, CZ Measurements performed under ISO/IEC 17025 accreditation; CAI, 521 | C |
| DSM Research, Geelen, NL Measurements performed under ISO/IEC 17025 accreditation; Lloyd's 65091 | C |
| European Commission, JRC, Institute for Reference Materials and Measurements (EC-JRC-IRMM), Geel, BE Measurements performed under ISO/IEC 17025 accreditation; BELAC, 268-TEST | H, S |
| Helmholtz Zentrum München, Deutsches Forschungszentrum für Gesundheit und Umwelt (GmbH), München, DE Measurements performed under ISO/IEC 17025 accreditation; DACH, DAC-PL-0141-01-10 | C |
| LGC Ltd., Teddington, UK Measurements performed under ISO/IEC 17025 accreditation; UKAS, 0003 | C |
| Milton, Treharne & Davis Limited, Cardiff, UK Measurements performed under ISO/IEC 17025 accreditation; UKAS, 0024 | C |

Activities: C: characterisation; H: homogeneity study, S: stability study

3. Processing of the materials

The channel sediment used for the production of BCR-320R originates from two different sampling sites (Site C is situated 500 m from the mouth of the Canal. Site D is situated at a dead end of the Side Canal D of the North Sea Canal which connects Amsterdam (NL) with the North Sea). Sediments from the two sites were combined to produce the material for BCR-320R.

Details about the processing can be found in [2].

4. Homogeneity

4.1. Between-bottle homogeneity

The between-bottle homogeneity is tested to ensure that the certified value is valid for all the produced bottles of the material, within the stated uncertainty.

For homogeneity testing of the Pb in the sediment material, 17 bottles of BCR-320R, selected at approximately regular intervals to cover the whole of the produced batches, were analysed. For assessment of homogeneity two sub-samples of each bottle were digested using HF and HNO₃ and analysed by ETAAS in triplicate (see Annex II). The results of these measurements were evaluated using a method described by Linsinger *et al.* [3].

The obtained data is first tested for normality of distribution. This is done by visual inspection of normal probability plots and histograms. Individual results followed an unimodal distribution. The combined uncertainty of the between-bottle measurement $u_{c,bb}$ is defined as the standard deviation of the results of the different bottles. u_{bb}^* is the inhomogeneity that could be hidden by the method repeatability.

$$u_{bb}^* = s_{meas} \sqrt{\frac{2}{n-1}}$$

The statistical treatment of the data obtained showed one outlying result for BCR-320R. There were no technical reasons to exclude this particular data, which is considered for further evaluation of the homogeneity contribution to the overall uncertainty.

The variation between bottles s_{bb} equals to $\sqrt{u_{c,bb}^2 - s_{meas}^2}$ if the argument under the root is valid. The uncertainty related to a possible between-bottle variation u_{bb} is then the larger of u_{bb}^* and s_{bb} .

The content of Pb in the BCR-320R was measured using ET-AAS. Tests showed that all the data obtained follow an unimodal distribution. The calculated results are displayed in Table 1.

Table 1: Results of the homogeneity study of Pb in BCR-320R

| Pb | Mean mass fraction [mg/kg] | S_{bb} [%] | S_{wb} [%] | u_{bb}^* [%] | u_{bb} [%] |
|----------|----------------------------|--------------|--------------|----------------|--------------|
| BCR-320R | 83.5 | MSB<MSW | 2.3 | 0.9 | 0.9 |

The degree of heterogeneity is considered fit for the purpose.

4.2. Micro-homogeneity, minimum sample intake

The micro-homogeneity of the BCR-320R was assessed using solid sampling ICP-MS. Sample intakes of 1 - 2 mg have been used.

The data (see Annex II) has been evaluated according to the following equation [4] and the sample masses are summarised in Table 2.

$$M = \left(\frac{k'_2 \cdot s_m}{u_{target}} \right)^2 \cdot m$$

where $k'_2 = 2.203$

$s_m = 6.45\%$

$u_{target} = 2.5\%$

$m = 1 \text{ mg}$

Table 2: Minimum sample mass for Pb in BCR-320R as determined by solid-sampling ICP-MS

| | |
|----------------------------|----------|
| Material | BCR-320R |
| Minimum sample intake [mg] | 32 |

An overall minimum sample intake of 100 mg was established for the sediment material based on the data for the other certified elements. It is evident that the calculated minimum sample intake for Pb is adequate and within the already set value.

5. Stability

5.1. Short-term stability

The short-term stability of the sediment material has been tested using an isochronous storage design [5]. Storage at 18 °C and 60 °C for 0, 1, 2 and 4 weeks have been tested, covering different conditions that can arise during transport. A temperature of -20 °C has been used as reference temperature for the isochronous storage design.

For the assessment of the short-term stability three sub-samples of each bottle were digested using HF and HNO₃ and analysed by ET-AAS in triplicate. The data points were plotted against time and the regression line was calculated. The plots can be found in Annex III.

In all cases the slope of the regression line was not found to be significantly different from zero. From the data obtained it can be concluded that the material is stable at elevated temperatures of up to 60 °C for up to 4 weeks. No special dispatching conditions are required.

5.2. Long-term stability

The long-term stability is tested to establish the shelf-life of the reference materials produced. It is tested for a certain period of time and expanded to the future. The long-term stability of the sediment material was assessed using the data obtained from the two characterisation studies in 2002 and 2007 and a dedicated study in 2009.

Only the accepted ID-ICP-MS and ID-TIMS data from the characterisation studies was used, thus ensuring the best comparability of the data sets. The dedicated study, conducted in 2009, used samples from the reference stock (stored at 4 °C) and samples from normal stock (stored at 18 °C). The method of choice for the determination of Pb was ET-AAS.

In order to ensure the successful comparison, the data were normalised to the mean of the respective t=0 study and then plotted against time. In this way, the long-term stability of the Pb in sediment materials was assessed over a period of 87 months. The uncertainty of stability u_{lts} of the materials is then calculated for the required shelf life as:

$$u_{lts} = \frac{RSD}{\sqrt{\sum (x_i - \bar{x})^2}} \cdot x$$

Table 3: Summary of relative uncertainty of stability U_{Its} for a shelf life of 87 months.

| Material | Shelf life at 18 °C [month] | U_{Its} [%] |
|----------|--------------------------------|------------------|
| BCR-320R | 87 | 0.7 |

The analyte content relative to the average of the study was plotted against time and the graph can be found in Annex III. A significant trend was found at a level of confidence of 95%, but not at 99%. This finding seems to be a statistical effect, since an outlying value was obtained in the 2009 data, resulting in high RSD of the data and lower mean value. A ratio comparison of the reference stock samples versus normal stock samples reveals a ratio of 1.02 ± 0.12 , proving the material's stability. Furthermore, the plotted time-points lie within the certified value. In addition, experience with the predecessor of this material, BCR-320, has proven the stability of such materials over at least 15 years.

6. Characterisation

The characterisation of the sediment material has been carried out using a laboratory intercomparison approach. The participants received two bottles of the material and were requested to provide 6 independent results, obtained on two different days. Different laboratories used different digestion methods as well as different methods for Pb determination. In addition, the water content had to be determined on separate sub-samples. The water content measurements had to be carried out by drying a sample of at least 1 g in a ventilated oven at 105 ± 2 °C for not less than 3 hours until constant weight was achieved.

6.1. Methods used

The selected laboratories employed HF in combination with other acid mixtures (HNO_3 , HClO_4 , H_3BO_3) for the digestion of the sediment material. Most of the laboratories used closed microwave digestion to turn the solid material into solution. Aqua regia oxidation with addition of HF on a hot plate and evaporation to dryness followed by filtration were among the other methods used.

The detection techniques used for the measurement of Pb in BCR-320R employed the ICP-AES, ICP-MS with and without Isotope dilution, as well as FAAS. The detailed method descriptions for the characterisation study are summarised in Annex I

As a quality control measure, the participants also received a bottle of BCR-277 (as a "unknown" sample). One result had to be provided for this sample. Individual results of the participants are displayed in Annex IV.

6.2. Evaluation of results

During the first characterisation exercise in 2002, a result for Pb obtained by one of the participating laboratories significantly differed from the rest, but no reasons were found to reject the result obtained. Consequently, the Pb content was not certified. Therefore a decision was taken to use completely different laboratories for the second characterisation.

All the datasets obtained during the characterisation study, organized in 2007, were subject to statistical outlier test (Grubbs single test, Grubbs double test). Based on this tests and visual inspection of the data, the result obtained by laboratory 4 is an outlier. Since there was no technical reason to exclude this dataset, it was retained for the calculation of the certified value and the associated uncertainty.

Laboratory 3, who used ICP-AES as a detection technique, admitted to encounter problems with the measurement of Pb, because of the high Fe content in the sediment material. They estimated that the high Fe content suppresses the signal for Pb of about 10-15%. Indeed, the obtained value for Pb was 15% lower than the value obtained by the same laboratory when using ICP-MS as a detection technique. In addition to that, the recovery for the certified value of the control sample was below 85%. Taking this as a technical reason, the result obtained by ICP-AES by laboratory 3 was excluded from the further statistical treatment of the obtained data sets.

All datasets used follow a unimodal distribution. Average and standard deviations are therefore meaningful estimates of the expected value and its variation.

The contribution of the characterisation to the uncertainty of the certified value is estimated as the standard error of the mean of the laboratory means. The mean of the laboratory means of the characterisation and the uncertainty of the characterisation u_{char} are listed in Table 4.

Table 4: Summary of data of the characterisation of BCR-320R

| Material | Number of valid datasets | Mean of laboratory means [mg/kg] | u_{char} [%] |
|----------|--------------------------|----------------------------------|----------------|
| BCR-320R | 6 | 84.6 | 2.4 |

7. Certified values and uncertainties

Certified values are calculated as the mean of the means of the laboratories. The respective combined standard uncertainty is calculated according to following equation, using relative uncertainties.

$$u_c = \sqrt{u_{bb}^2 + u_{lts}^2 + u_{char}^2}$$

The expanded uncertainty of the certified values U_{CRM} is calculated with a coverage factor of $k = 2$, representing a level of confidence of approximately 95 %. Results are listed in Table 5.

Table 5: Certified value and relevant uncertainty for BCR-320R. The certified value refer to dry mass.

| Material | Number of valid data sets | Certified value [mg/kg] | U_{CRM} [mg/kg], $k = 2$ | u_{char} [%] | u_{bb} [%] | u_{lts} [%] |
|----------|---------------------------|-------------------------|----------------------------|----------------|--------------|---------------|
| BCR-320R | 6 | 85 | 5 | 2.4 | 0.9 | 0.7 |

7.1. Metrological traceability

Traceability of the certified values to the SI is ensured through the set-up of the characterisation. The methods used for the characterisation of Pb in sediment materials consist of isotope dilution technique in combination with ICP-MS, ICP-AES and FAAS. In addition, different calibrants have been used, which are all certified reference materials, traceable to the SI. The participating laboratories used calibrated balances and different methods for the sample preparation, including different sample intakes, acid mixtures and digestion strategies (Annex I).

7.2. Commutability

Commutable CRMs must exhibit the same analytical behaviour for given methods as a real laboratory sample. The majority of the laboratories participating in the characterisation study provided a large variety of different digestion and detection methods, demonstrating potential to give similar results. The good agreement between the results obtained shows the commutability of the material. Nevertheless it has to be kept in mind that the certified reference material might show a different behaviour in particular during digestion, due to their small particle sizes in contrast to the possibly larger particle sizes encountered for real laboratory samples, and the intensive processing that this material has undergone.

8. Instructions for use

The bottles should be shaken for at least two minutes before opening to ensure re-homogenisation of the content.

The certified value refers to dry mass. A dry mass determination should always be carried out on separate sub-samples.

The dry mass determination should be carried out by drying a sample of at least 1 g in a ventilated oven at 105 ± 2 °C until constant weight is achieved, but for not less than 3 hours. Samples should be cooled down in a desiccator.

A minimum sample intake of 100 mg for BCR-320R is recommended.

Samples can be stored at room temperature. Care should be taken to avoid moisture pick up once the bottles are opened.

9. References

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Annex I: Summary of methods used

Table 7: Summary of the methods used for the characterisation of Pb in BCR-320R.

| Lab code/year | Method acronym | Sample mass (g) | Sample preparation | Calibrants | Instrumentation and measurement method |
|---------------|----------------|-----------------|--|--|---|
| 01/2002 | ICP-MS-ID | 0.1 | Closed vessel pressure digestion, using 4 mL HF and 3 mL HNO ₃ , overnight in heating block, 200 °C, 4 h in oven, 200 °C | Isotopically enriched spike NIST SRM 991 (Pb) | ICPMS (Q) Ratios measured: ²⁰⁸ Pb / ²⁰⁶ Pb, |
| 03/2002 | ID-TIMS | 0.5 | Wet digestion, 10 mL HNO ₃ , 5 ml HF (48h, 180 °C), evaporation to dryness, 2 ml HClO ₄ , 7 ml HNO ₃ (5h, 100 °C), Separation of Pb by anion exchange. | Isotopically enriched metal NIST SRM 3158 (Pb) | TIMS with single Faraday-cup detection, using a single Re filament, H ₃ PO ₄ / Silicagel matrix Ratios measured: ²⁰⁸ Pb / ²⁰⁴ Pb |
| 06/2002 | ICP-MS-ID | 0.1 | Microwave digestion 3 mL HNO ₃ , 1 mL HCl, 1 mL HF | NIST SRM 981 (Pb) | ICPMS (Q) Ratios measured: ²⁰⁸ Pb / ²⁰⁶ Pb |
| 01/2007 | ICP-MS-ID | 0.2 | 6 mL HNO ₃ , 2 mL HCl, 2 mL HF closed vessel microwave digestion | NIST SRM 981 (primary standard Pb), NIST SRM 983 (spike Pb) | ICPMS (Q) Ratios measured: ²⁰⁸ Pb / ²⁰⁶ Pb |
| 01/2007 | ICP-MS-ID | 0.2 | closed microwave digestion (30 bar) with 6 mL HNO ₃ , 2 mL HCl, 2 mL HF; | Primary standard: NIST SRM981, gravimetrically diluted in 1% HNO ₃ Spike: NIST SRM 983 | Agilent 7500ce CRC-ICPMS Ratios measured: ²⁰⁸ Pb / ²⁰⁶ Pb |
| 02/2007 | ICP-MS | 0.3 | Closed microwave digestion with 15 mL HNO ₃ (65%) and 1.5 mL HF (40%) | External calibration (5 points range 0-50 µg/L); Internal standard: Lu at m/z=175 | Quantification of Pb by ICP-MS at m/z=206, m/z=207 and m/z=208, the results are the average of three isotopes |
| 03/2007 | ICP-AES | 0.15 | Closed microwave digestion (60 bar) with 1,5 mL HNO ₃ ; 4,5 mL HCl and 1 mL HF at 1400W for 30 min. Then addition of 5 mL H ₃ B ₃ O ₃ and microwaved using the same programme. | Single element standard. Calibration external 0, 2.5, 5.0, 10, 25, 50, 100, 250, 500 and 1000 µg/L standards, | ICP-AES at 220,353 nm line |

| Lab code/year | Method acronym | Sample mass (g) | Sample preparation | Calibrants | Instrumentation and measurement method |
|---------------|----------------|-----------------|---|--|--|
| | ICP-MS | 0.15 | Samples diluted to 30 mL with water. | NIST SRM 3128 | ICP-MS Low resolution: Pb at m/z=208 |
| 04/2007 | FAAS | 1.0 | Wet oxidation with aqua regia (6 mL HCl: 2 mL HNO ₃) and 2 mL HF in PTFE beakers followed by digestion and reduction with gentle heating on a hot-plate; sample intake about 1 g; quantification by flame AAS. Results corrected to dried from moisture content (upon 1 g to constant mass, as specified) | Calibration was with comparison to external 0, 0.5, 2.0, 5.0 and 10.0 mg/L standards, which provided linear calibration. | FAAS, Deuterium correction, wavelengths: Pb 283.3 nm |
| 05/2007 | ICP-AES | 0.5 | Twice evaporation nearly to dryness with 10 mL HF and 5 mL HNO ₃ . Sample finally dissolved in 30 mL 5% HNO ₃ and after filtration made up to 100 mL with water. | | ICP-AES at 220,353 nm line |
| | ICP-MS | 0.5 | | | ICP-MS (Q) Isotopes measured: ²⁰⁶ Pb, ²⁰⁷ Pb, ²⁰⁸ Pb |

Table 8: Summary of the methods used for the homogeneity, short-term and long-term stability studies.

| Method acronym | Sample mass (g) | Sample preparation | Calibrant | Instrumentation and measurement method |
|----------------|-----------------|---|---|--|
| ETAAS | 0.1 | Microwave digestion, using 10 mL mixture of 5% HF and 20% HNO ₃ , 220 °C, 100 bar, 2 h | Merck single element standard, Pb 1000 mg/kg, external calibration 20, 30, 40 and 50 µg/L | ETAAS, Analytic Jena 650 |

Annex II: Data from homogeneity study

Table 9: Homogeneity data for BCR-320R measured by ETAAS.

| Bottle number | Analytical sequence | Replicate 1 Result (mean of tree) [mg/kg] | Analytical sequence | Replicate 2 Result (mean of tree) [mg/kg] | Sample Mean [mg/kg] |
|---------------|---------------------|--|---------------------|--|------------------------|
| 90 | 6 | 83.5 | 31 | 83.4 | 83.5 |
| 310 | 20 | 82.4 | 33 | 82.5 | 82.4 |
| 530 | 1 | 83.2 | 27 | 81.2 | 82.2 |
| 750 | 4 | 83.1 | 30 | 81.8 | 82.5 |
| 970 | 24 | 82.6 | 10 | 84.1 | 83.4 |
| 1190 | 14 | 86 | 19 | 83.2 | 84.6 |
| 1410 | 15 | 87.2 | 25 | 80.6 | 83.9 |
| 1630 | 23 | 82.2 | 5 | 82.4 | 82.3 |
| 1850 | 22 | 83.1 | 34 | 81.9 | 82.5 |
| 2070 | 11 | 83.6 | 18 | 83.8 | 83.7 |
| 2290 | 32 | 82.9 | 8 | 83.6 | 83.2 |
| 2510 | 12 | 84.7 | 21 | 83.9 | 84.3 |
| 2730 | 28 | 82.2 | 16 | 85.4 | 83.8 |
| 2972 | 7 | 84.4 | 29 | 82.3 | 83.4 |
| 3190 | 13 | 89.2 | 3 | 83.9 | 86.5 |
| 3410 | 17 | 86.2 | 2 | 82.1 | 84.2 |
| 3630 | 9 | 82.2 | 26 | 82 | 82.1 |

Table 10: Data from micro-homogeneity study for BCR-320R, measured by solid-sampling ICP-MS.

| Bottle number | 2625 | 2317 | 1855 | 1392 | 2009 | 1700 | 776 | 3856 | 1238 | 622 | 314 | 6 |
|---------------|------|------|------|------|------|------|------|------|------|------|------|------|
| PA-norm | 1.01 | 1.04 | 1.00 | 1.01 | 1.38 | 1.08 | 1.00 | 1.05 | 1.08 | 1.02 | 0.98 | 1.05 |
| | 1.05 | 1.08 | 1.05 | 1.15 | 1.06 | 1.06 | 1.00 | 1.06 | 1.00 | 1.02 | 1.10 | 0.98 |
| | 0.97 | 1.01 | 1.07 | 1.11 | 1.13 | 1.00 | 0.98 | 0.94 | 0.95 | 1.08 | 1.14 | 1.04 |
| | 1.09 | 1.15 | 1.00 | 1.02 | 1.01 | 1.08 | 1.14 | 1.04 | 0.95 | 1.09 | 1.03 | 1.12 |
| | 0.97 | 1.04 | 1.02 | 1.02 | 1.01 | 0.99 | 0.98 | 0.98 | 0.98 | 0.96 | 1.08 | 0.97 |
| | 1.05 | 1.12 | 1.07 | 1.17 | 1.08 | 1.05 | 1.05 | 0.95 | 1.04 | 1.07 | 1.08 | 0.94 |
| | 0.86 | 1.13 | 0.97 | 1.04 | 1.10 | 0.95 | 1.10 | 0.97 | 1.22 | 1.09 | 1.11 | 1.13 |
| | 1.02 | 0.99 | 1.06 | 1.07 | 1.12 | 1.06 | 1.08 | 1.12 | 1.00 | 1.06 | 1.08 | 1.08 |
| | 1.01 | 1.03 | 1.00 | 1.03 | 1.22 | 1.05 | 0.99 | 1.00 | 1.00 | 1.08 | 1.00 | 0.92 |
| | 1.08 | 1.17 | 1.01 | 1.08 | 1.23 | 0.96 | 0.94 | 1.10 | 1.00 | 1.07 | 1.05 | 1.18 |
| n | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 |
| Mean | 1.01 | 1.08 | 1.03 | 1.07 | 1.13 | 1.03 | 1.03 | 1.02 | 1.02 | 1.05 | 1.07 | 1.04 |
| RSD | 0.07 | 0.06 | 0.03 | 0.05 | 0.10 | 0.05 | 0.06 | 0.06 | 0.08 | 0.04 | 0.05 | 0.08 |

Annex III: Data from stability study

Short-term stability

Figure 1: Short-term stability graph for Pb in BCR-320R at 18 °C. Reference samples stored at -20 °C.

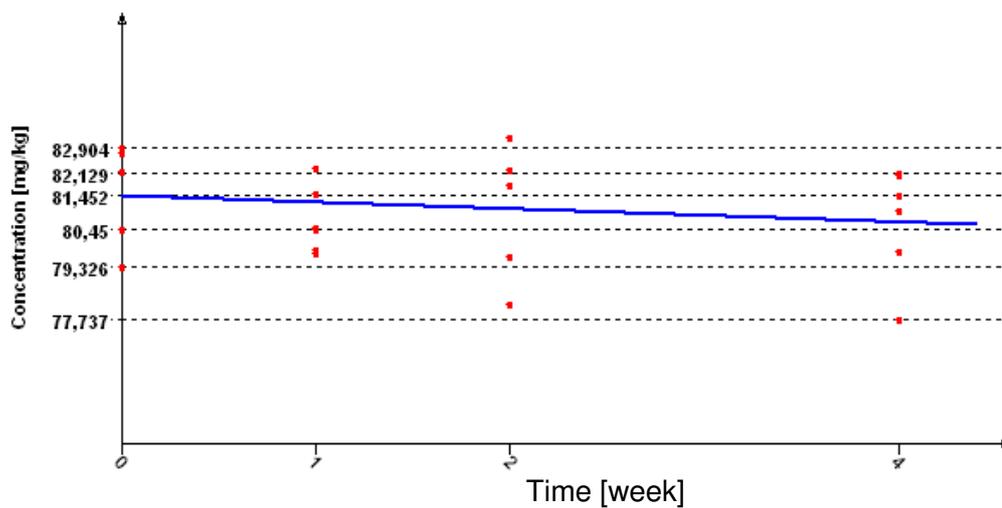
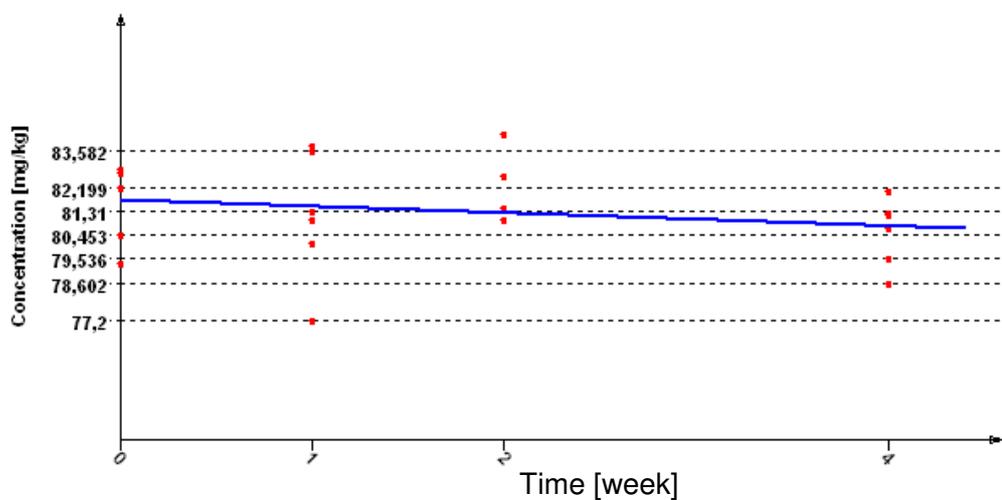
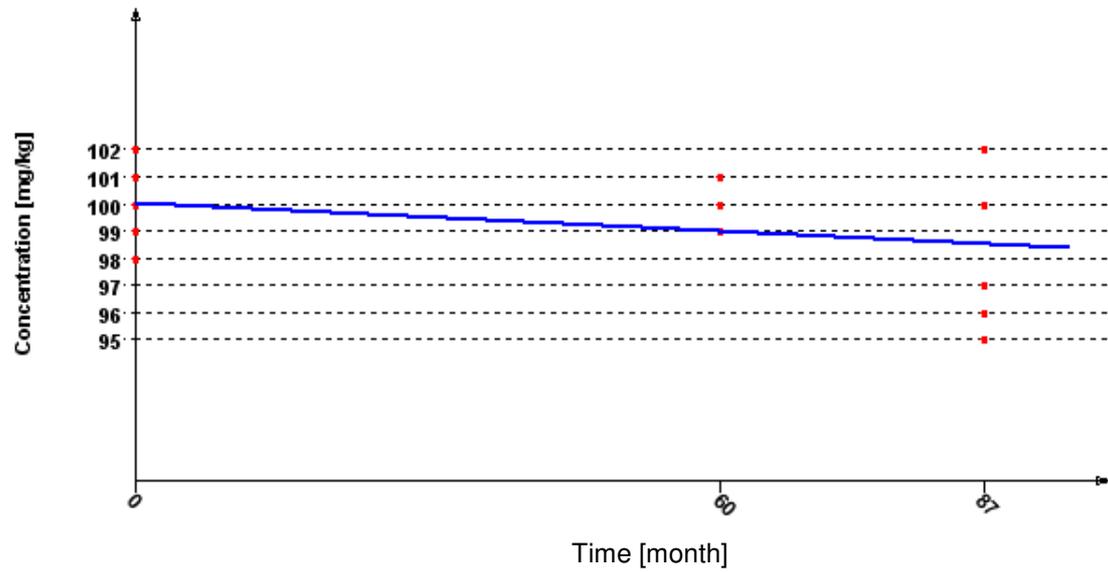


Figure 2: Short-term stability graph for Pb in BCR-320R at 60 °C. Reference samples stored at -20 °C.



Data from long-term stability studies:

Figure 3: Long-term stability graph for Pb in BCR-320R at 18 °C



Annex IV: Data from characterisation study

Table 11: Results BCR-320R, Pb

| Lab code | Method acronym | Results of the replicate measurements [mg/kg] | | | | | | Mean [mg/kg] | Standard deviation [mg/kg] |
|----------|----------------|---|-------|-------|-------|------|-------|--------------|----------------------------|
| | | | | | | | | | |
| 01/2007 | ICP-MS-ID | 86.25 | 87.89 | 86.98 | 86.57 | 86.5 | 87.46 | 86.94 | 0.63 |
| 02/2007 | ICP-MS | 87.4 | 85 | 87.9 | 84.7 | 86.8 | 88 | 86.63 | 1.45 |
| 03/2007 | ICP-MS | 85.1 | 86 | 86.1 | 82.3 | 83.3 | 84 | 84.47 | 1.53 |
| 04/2007 | FAAS | 76 | 75.2 | 72.7 | 75.9 | 80.8 | 72.7 | 75.55 | 2.98 |
| 05/2007 | ICP-AES | 90.4 | 93 | 84.9 | 89.9 | 90.2 | 89.7 | 89.68 | 2.63 |
| 05/2007 | ICP-MS | 86.4 | 83.8 | 82.1 | 84.9 | 84.2 | 83.3 | 84.12 | 1.46 |

Figure 5: Laboratory means BCR-320R, Pb. Dots represent the individual results as reported by the participating laboratories (- mean of laboratory means, -- expanded uncertainty of the mean value)

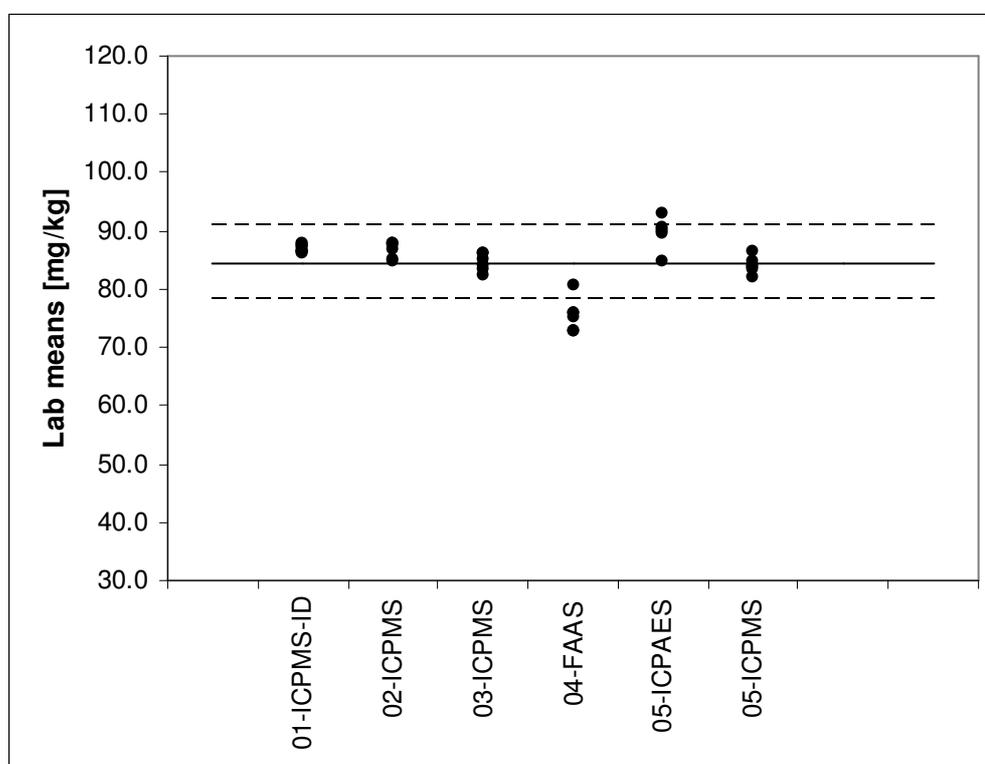


Table 12: Results BCR-277 (unknown control sample), Pb.

| Lab code | Method acronym | Certified value [mg/kg] | Measured result [mg/kg] | Recovery [%] |
|----------|----------------|-------------------------|-------------------------|--------------|
| 01/2007 | ID-ICP-MS | 146 | 148.7 | 101.8 |
| 02/2007 | ICP-MS | 146 | 144.8 | 99.2 |
| 03/2007 | ICP-OES | 146 | 115 | 78.8 |
| 03/2007 | ICP-MS | 146 | 132.7 | 90.9 |
| 04/2007 | FAAS | 146 | 124.9 | 85.5 |
| 05/2007 | ICP-OES | 146 | 127.3 | 87.2 |
| 05/2007 | ICP-MS | 146 | 126.8 | 86.8 |

European Commission

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Abstract

This report describes the additional certification of Pb in BCR-320R (channel sediment). This material has already been certified for its total trace element content (As, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Sc, Th, Tl, U, V and Zn. Indicative values have been established for Se and Sn).

Difficulties with the characterisation of Pb made an additional certification necessary. During the first characterisation exercise in 2002, a result for Pb obtained by one of the participating laboratories significantly differed from the rest, but no reasons were found to reject the result obtained. Therefore a decision was taken to use completely different laboratories for the present characterisation.

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