



Institute for Reference
Materials and Measurements



CERTIFICATION REPORT

The Certification of the Mass Fractions of Arsenic,
Cadmium, Nickel and Lead in Fine Dust (PM₁₀-like matrix)

Certified Reference Material ERM[®]-CZ120

EUR 24577 EN – 2010

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**The Certification of the Mass Fractions of Arsenic,
Cadmium, Nickel and Lead in Fine Dust (PM₁₀-like matrix)**

Certified Reference Material ERM[®]-CZ120

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Summary

This report describes the preparation and certification of the new Reference Material (CRM) ERM-CZ120, which is a PM₁₀-like fine dust, certified for the elements arsenic, cadmium, nickel and lead.

Certification of the CRM included testing of the homogeneity and stability of the material as well as the characterisation using an intercomparison approach.

The main purpose of the material is to assess method performance, i.e. for checking accuracy of analytical results in the field of air quality control/measurement. As any reference material, it can also be used for control charts or validation studies.

The certified values are listed below:

Element	Mass Fraction	
	Certified value ¹⁾ [mg/kg]	Uncertainty ²⁾ [mg/kg]
Arsenic	7.1	± 0.7
Cadmium	0.90	± 0.22
Lead	113	± 17
Nickel	58	± 7

¹⁾ The value is the unweighted mean of accepted sets of data, each set being obtained in a different laboratory and/or with a different method. The certified values are reported on mass of the sample after conditioning the sample using conditions as described in EN12341 and are traceable to the SI.
²⁾ Expanded uncertainty with a coverage factor $k = 2$ according to the Guide to the Expression of Uncertainty in Measurement (GUM), corresponding to a level of confidence of about 95 %.

Additional material information is listed below:

Element	Mass fraction	Element	Mass fraction
	Value [mg/kg]		Value [mg/kg]
Aluminium	34100 ¹⁾	Molybdenum	33.2 ²⁾
Antimony	64.7 ²⁾	Neodymium	22.2 ¹⁾
Barium	562.2 ²⁾	Potassium	10998 ²⁾
Bromine	10.2 ²⁾	Rubidium	52.3 ²⁾
Caesium	3.1 ²⁾	Samarium	4.1 ²⁾
Calcium	63043 ²⁾	Scandium	7.4 ²⁾
Cerium	56.8 ²⁾	Silicon	229000 ⁴⁾
Chlorine	10033 ¹⁾	Sodium	14211 ²⁾
Chromium	201 ²⁾	Strontium	251 ²⁾
Cobalt	14.3 ²⁾	Tantalum	1.0 ²⁾
Copper	462 ¹⁾	Terbium	0.6 ²⁾
Dysprosium	3.3 ¹⁾	Thorium	7.0 ²⁾
Elemental carbon	45433 ³⁾	Titanium	4372 ¹⁾
Europium	0.8 ²⁾	Total carbon	111333 ³⁾
Gallium	8.7 ¹⁾	Total organic carbon	76633 ³⁾
Gold	0.02 ¹⁾	Tungsten	4.1 ¹⁾
Hafnium	8.4 ²⁾	Uranium	2.6 ²⁾
Iron	38144 ²⁾	Vanadium	72.4 ¹⁾
Lanthanum	25.0 ²⁾	Ytterbium	1.7 ²⁾
Magnesium	13200 ¹⁾	Zinc	1240 ²⁾
Manganese	611 ¹⁾	Zirconium	341 ²⁾

¹⁾ The mass fraction represents the mean value of two results provided by two laboratories. The measurements were performed by k_0 -NAA.

²⁾ The mass fraction represents the mean value of six individual results provided by one laboratory. The measurements were performed by k_0 -NAA.

³⁾ The mass fraction represents the mean value of three individual results provided by one laboratory. The results were obtained by coulometric titration.

⁴⁾ The mass fraction represents the mean value of three individual results provided by one laboratory. The results were obtained by X-ray fluorescence spectroscopy.

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Glossary

ANOVA	Analysis of variance
AQUILA	National Air Quality Reference Laboratories
AFS	Atomic Fluorescence Spectrometry
BCR	Community Bureau of Reference
CRM	Certified Reference Material
DG ENV	Directorate General for the Environment
DLS	Dynamic Light Scattering
EC	European Commission
ERM	European Reference Material
FAAS	Flame Atomic Absorption Spectrometry
HG	Hydride Generation
ICP	Inductively coupled plasma
IES	Institute for Environment and Sustainability
IRMM	Institute for Reference Materials and Measurements
JRC	Joint Research Centre
MS_{between}	Mean square between bottles from an ANOVA
MS_{within}	Mean square within a bottle from an ANOVA
n	Average number of replicates per bottle
NIST	National Institute of Standards and Technology
OES	Optical Emission Spectrometry
PAH	Polycyclic aromatic hydrocarbon
PM	Particulate matter
PM_{10}	Particulate matter of 10 μm and less aerodynamic diameter
PSA	Particle size analysis
QMS	Quadrupole Mass Spectrometry
Q3	Percentage distribution of the particles
$q3^*$	Volume distribution of the particles
Q_x	Cumulative distribution equal x vol. %
RM Unit	Reference Materials Unit
<i>RSD</i>	Relative standard deviation
s	Standard deviation
s_{bb}	Standard deviation between-units
s_f	Precision of response measurement
SFMS	Sector field mass spectrometry
TSP	Total Suspended Particulate
u_{bb}	Standard uncertainty related to a possible between-bottle heterogeneity
u_{char}	Standard uncertainty on characterisation
U_{CRM}	Expanded uncertainty of the certified value
u_{hom}	Standard uncertainty on homogeneity
u_{stab}	Standard uncertainty on stability
U_{bb}	Maximum heterogeneity that could be hidden by method repeatability
V-KFT	Volumetric Karl-Fischer titration
$V_{MS_{\text{within}}}$	Degrees of freedom of MS_{within}
XRF	X-ray fluorescence

The subscript "rel" is added when a variable is expressed in relative terms (e.g. as percent).

1. Introduction

The European Air Quality Directives, specifically 2008/50/EC [1] and 2004/107/EC [2], require the monitoring of arsenic, cadmium, nickel, lead and several polycyclic aromatic hydrocarbons (PAHs) in PM₁₀ (particulate matter of 10 µm and less aerodynamic diameter) in ambient air. Laboratories in the Member States have to carry out measurements of the aforementioned analytes to verify compliance with target and limit values set in the Directives. Therefore, appropriate quality control tools need to be available to ensure the quality of measurement data. Certified Reference Materials (CRMs) and proficiency testing schemes are such essential tools for analytical quality control and checking of laboratory proficiency and data comparability. Currently, no suitable CRM is available with certified contents of arsenic, cadmium, nickel, lead and polycyclic aromatic hydrocarbons in a matrix that would sufficiently resemble airborne particulate matter (PM₁₀). Likewise, there is a lack of suitable quality control samples for the organisation of proficiency testing schemes as currently carried out by the JRC-IES (Joint Research Centre, Institute for Environment and Sustainability) for atmospheric pollutants.

Therefore, the feasibility of the production of Certified Reference Materials for arsenic, cadmium, nickel, lead and PAHs were evaluated at JRC IRMM (Joint Research Centre, Institute for Reference Materials and Measurements), funded by DG ENV (Directorate General for the Environment) [3]. The positive outcome of the feasibility study allowed for the production and certification of two CRMs, one for arsenic, cadmium, nickel, lead (ERM-CZ120) and one for selected PAHs (ERM-CZ100). The production and certification of the former is described in this report. This work was supported by funding of DG ENV.

2. Participants

2.1 Project management and evaluation

European Commission, Joint Research Centre, Institute for Reference Materials and Measurements (IRMM), Geel, BE
(accredited to ISO Guide 34 for production of certified reference materials, BELAC No 268-TEST)

2.2 Processing

European Commission, Joint Research Centre, Institute for Reference Materials and Measurements (IRMM), Geel, BE
(under current scope of ISO Guide 34 accreditation; BELAC No 268-TEST)

2.3 Homogeneity and stability studies

The Food and Environment Research Agency (FERA), York, GB
(accredited to ISO/IEC 17025, UKAS No 1642)
ALS Scandinavia AB, Luleå, SE
(accredited to ISO/IEC 17025, SWEDAC No 1087)
National Physical Laboratory (NPL), Teddington, GB
(accredited to ISO/IEC 17025, UKAS No 0002)

2.4 Characterisation study

Agencija Republike Slovenije za Okolje, Ljubljana, SI
(accredited to ISO/IEC 17025, SA No LP-030)
Eesti Keskkonnauuringute Keskus OÜ, Tallinn, EE
(accredited to ISO/IEC 17025, EAK L008)
Energieonderzoek Centrum Nederland (ECN), Petten, NL
(accredited to ISO/IEC 17025, RvA No L135)
Executive Environment Agency, Sofia, BG
(accredited to ISO/IEC 17025, BAS, N°32-testing laboratory)
Helmholtz Zentrum München - Deutsches Forschungszentrum für Gesundheit und Umwelt (GmbH), Neuherberg, DE
(accredited to ISO/IEC 17025, DAC-PL-0141-01-10)
Institut National de l'environnement industriel et de risques (INERIS), Verneuil-en-Halatte, FR
(accredited to ISO/IEC 17025, COFRAC-Accreditation 1-0157)
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National Physical Laboratory (NPL), Teddington, GB
(accredited to ISO/IEC 17025, UKAS No 0002)
Rijksinstituut voor Volksgezondheid en Milieu (RIVM), Bilthoven, NL
(accredited to ISO/IEC 17025, RvA No L408)
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(accredited to ISO/IEC 17025, BELAC No 045-TEST)
Vlaamse Milieumaatschappij VMM, Antwerpen, BE,
Studiecentrum voor Kernenergie - Centre d'Etude de l'énergie Nucléaire (SCK-CEN), Mol, BE
(accredited to ISO/IEC 17025, BELAC No 015-TEST)
The Food and Environment Research Agency (FERA), York, GB
(accredited to ISO/IEC 17025, UKAS No 1642)
Wojewódzki Inspektorat Ochrony Środowiska we Wrocławiu, Wrocław, PL
(accredited to ISO/IEC 17025, PCA, AB 075)
Wojewódzki Inspektorat Ochrony Środowiska we Wrocławiu delegatura w Jeleniej Górze, Jelenia Góra, PL
(accredited to ISO/IEC 17025, PCA, AB 075)

2.5 Additional characterisation

Umweltbundesamt GmbH, Wien, AT
Państwowy Instytut Geologiczny, Warszawa, PL
(accredited to ISO/IEC 17025, PCA, AB 283)

3. Processing of the material

3.1 Feasibility study

A feasibility study of the production of CRMs for arsenic, cadmium, nickel, lead and PAHs in a PM₁₀-like matrix was performed. Within the frame of the study, four materials were evaluated in order to determine whether they are suitable for the production of the air quality CRMs: BCR-723 (a road dust certified for palladium, platinum and rhodium), BCR-605 (an urban road dust certified for trimethyllead), winter and summer filter dust (TSP (Total Suspended Particulate) collected from the ventilation system of IRMM buildings) and tunnel dust (TPS collected from the walls of the road tunnel "Wisłostrada" in Warsaw).

The materials were tested for particle size distribution, content of the analytes, homogeneity and short-term stability. It was found that the summer filter dust, the winter filter dust and the tunnel dust could be used for production of CRMs [3].

However, the tunnel dust material was selected for the production and certification of the elements and PAHs because the amount of this material (~12 kg) was sufficient for this purpose while for the filter dust additional material collection would have to be performed.

3.2 Processing of the tunnel dust material

The material originates from the road tunnel "Wisłostrada" in Warsaw, Poland. The tunnel is approximately 900 m in length and is a major traffic route through the city. The dust was collected mainly from the tunnel walls and partly from the tunnel sidewalks inaccessible to people. The material was separated from the coarse particles by sieving (0.5 mm sieve followed by 0.250 mm sieve) and then ground using a jet mill to finally obtain a very fine dust with 10 vol.% of particles below 1.75 µm, 16 vol.% of particles below 2.49 µm, 50 vol.% of particles below 7.59 µm, 84 vol.% of particles below 15.01 µm and 90 vol.% of particles below 20 µm (see Table 1) [4]. The resulting material was stored at 4 °C to avoid losses of volatile analytes.

Table 1: Particle size distribution of the starting material, tunnel dust

Tunnel dust	Upper particle size ± expanded uncertainty ^a [µm]					
	Q ₁₀ ^b	Q ₁₆ ^b	Q ₅₀ ^b	Q ₈₄ ^b	Q ₉₀ ^b	Q ₁₀₀ ^b
	1.75 ± 0.08	2.49 ± 0.10	7.59 ± 0.33	15.01 ± 0.72	17.57 ± 0.84	73

^a: as measured using DLS (Dynamic Light Scattering) with a coverage factor $k = 2$ corresponding to a level of confidence of about 95 %

^b: Q₁₀, 16, 50, 84, 90, and 100 – cumulative distribution equals 10 vol.%, 16 vol.%, 50 vol.%, 84 vol.%, 90 vol.% and 100 vol.%, respectively

Airborne particles have irregular shapes, and their aerodynamic behaviour is expressed in terms of the diameter of an idealised spherical particle known as aerodynamic diameter. Particles are sampled and described on the basis of their aerodynamic diameter, which is usually simply referred to as particle size. However, particles having the same aerodynamic diameter may have different dimensions and shapes. For practical purpose, particle size distribution were measured by DLS in a dispersion and are only indicative of the aerodynamic diameter of the particles.

Particle size measurements were performed in the PSA (Particle Size Analysis) laboratory of the RM Unit, IRMM. The measurements were performed using a laser light diffraction technique, device: SYMPATEC Helos (Clausthal-Zellerfeld, Germany) equipped with 50 mL

cuvette, dispersant: 2-propanol, measurement time: 10 s, stirrer rate: 1200 revolutions per minute.

The results are presented in Figure 1.

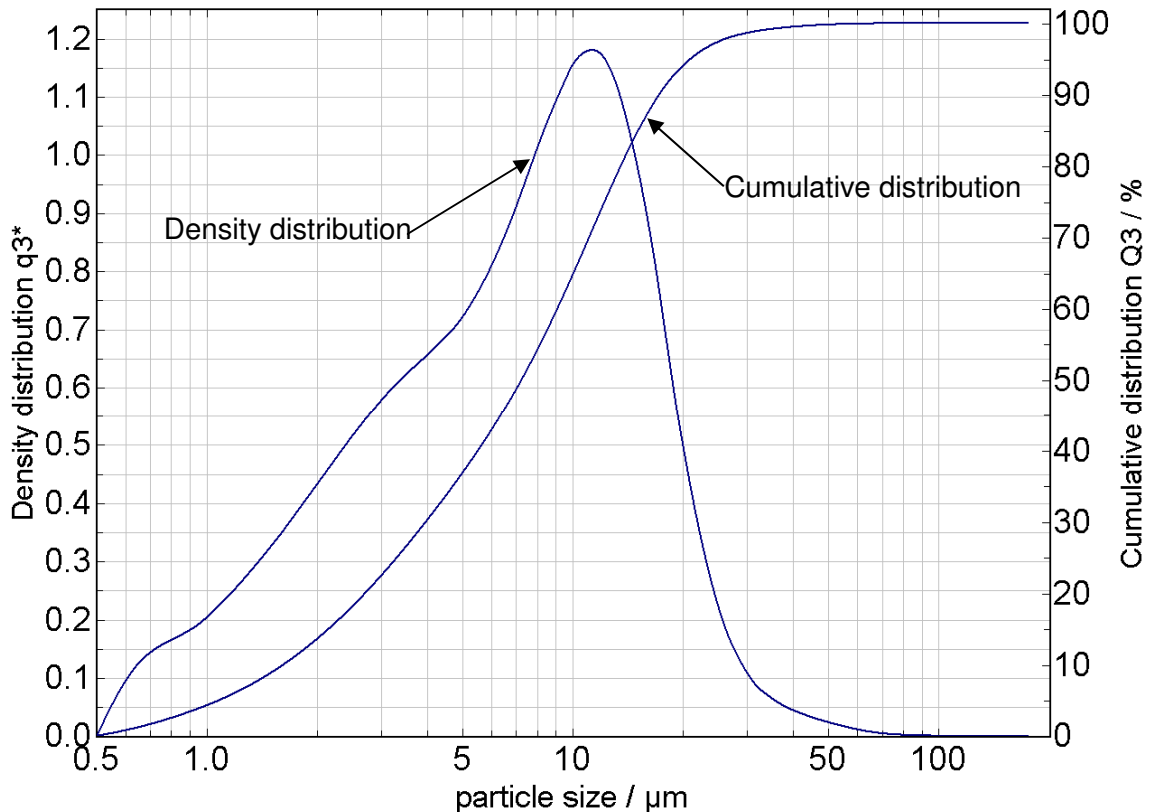


Figure1: Particle size distribution (in vol. %)

The density curve gives the volume distribution (q_3^*) of the particles as a function of the equivalent sphere diameter. The cumulative curve shows percentage distribution (Q_3) as a function of the particles diameters.

To investigate the material morphology the micrographs were taken. In order to take the micrographs a portion of dust was deposited on a stub covered with an adhesive carbon tape. Then it was coated with gold for 2 minutes at 20 mA (Emitech K550X Sputter Coater), corresponding to a nominal gold layer thickness of 15 nm. The micrographs were obtained using a Zeiss microscope Stemi 2000-C (PSA laboratory of the RM Unit, IRMM) and an electron microscope: dual-beam FIB-SEM Quanta 200/3D (Engineering Materials Laboratory of the RM Unit, IRMM).

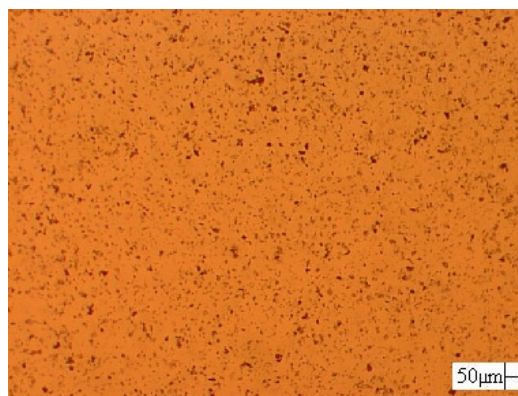


Figure 2: Micrographs obtained using a Zeiss microscope Stemi 2000-C

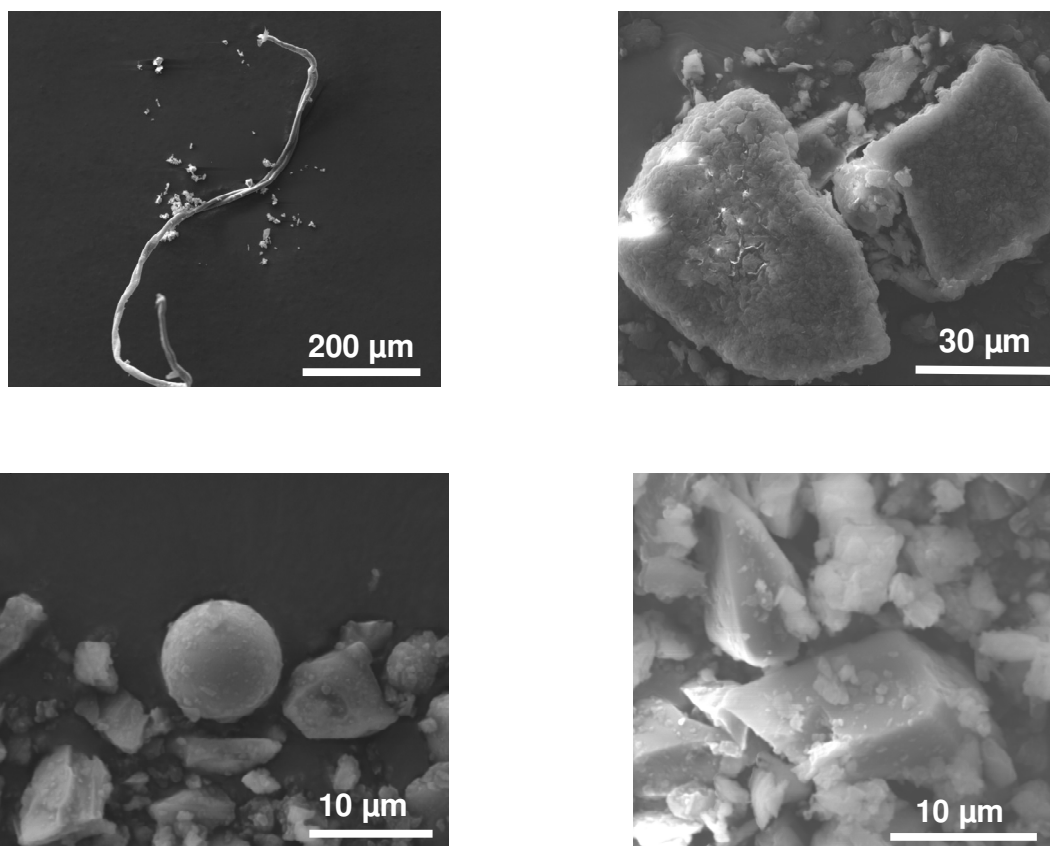


Figure 3: Micrographs with different magnifications obtained using an electron microscope dual-beam FIB-SEM Quanta 200/3D

A typical material morphology is shown in Figure 2. Micrographs were obtained using a Zeiss microscope Stemi 2000-C. In Figure 3 (smaller and larger magnifications), the images show different structures found in the material that are not representative of the bulk material. As shown, the material consists of a large variety of particles (spheres, cubes, fibres, irregular shapes).

The water content determined in the final product using volumetric Karl Fischer titration (V-KFT, Metrohm Ltd, Herisau, CH) was 2.68 % (m/m) \pm 0.30 % (m/m) (average of three measurements on ten vials, expanded uncertainty with a coverage factor of $k = 2$).

Material filling

The material was filled into 5 ml amber glass vials, closed with a rubber stopper (coated with PTFE) and an aluminium cap under argon atmosphere. Each vial contained about 0.5 g of the material.

4. Homogeneity study

4.1 Between-bottle homogeneity

The between-bottle homogeneity was evaluated to ensure that the certified values of the CRM are valid for all vials of the material, within the stated uncertainty.

For the homogeneity test, eighteen bottles of the material were selected using a random stratified sampling scheme. The number of selected vials corresponds to approximately the cubic root of the total number of the produced units.

From each bottle, three independent replicates (about 150 mg sample intake) were prepared by digestion in a microwave oven using 4 ml HNO₃ and 1 ml HCl. The samples were analysed by means of inductively coupled plasma-mass spectrometry (ICP-QMS) for the determination of Cd, Ni and Pb and ICP-QMS with collision cell (helium mode) for As determination.

The results were not corrected for the water content. The results (mass fractions) were reported on mass of the sample after conditioning the sample using conditions as described in [5]. This means that before analysis, the sample had to be opened and kept for at least 48 h in the air-conditioned weighing room with a temperature of 20 °C ± 1 °C and a relative humidity of 50 % ± 5 % to reach equilibrium under weighing room conditions.

The measurements were carried out in a random sequence to be able to separate a potential analytical drift from a trend in the filling sequence.

On the obtained data, Grubbs-tests were performed to detect outlying individual results and outlying bottle averages.

No outlying individual results or outlying bottle averages were found.

Consequently, regression analyses were performed to evaluate potential trends in the analytical sequence and trends in the filling sequence. In cases of Cd, Ni and Pb, for both the analytical sequence and the filling sequence no trends were found.

In case of As, a trend in the analytical sequence was found. Since the uncertainty of homogeneity was very low for As (see Table 4) and drift correction would not significantly affect the uncertainty, drift correction was not applied.

The obtained data were first tested whether they follow a normal, or at least unimodal distribution. This was done by visual inspection of normal probability plots and histograms (if the data do not follow at least a unimodal distribution, the calculation of standard deviations would be inappropriate). All individual results were normally and unimodally distributed.

The results were then evaluated by a one-way analysis of variance (ANOVA). From the results of the ANOVA calculation, the following figures were determined:

Between-bottle standard deviation (s_{bb}) as given by:

$$s_{bb} = \sqrt{\frac{MS_{\text{between}} - MS_{\text{within}}}{n}}, \quad (1)$$

where:

MS_{between} : mean squares between-bottle from an ANOVA

MS_{within} : mean squares within-bottle from an ANOVA

n : average number of replicates per vial

The maximum heterogeneity that can be hidden by the method repeatability (which is used as the minimum uncertainty contribution from homogeneity) is defined by:

$$u_{bb}^* = \sqrt{\frac{MS_{\text{within}}}{n}} \sqrt[4]{\frac{2}{v_{MS_{\text{within}}}}}, \quad (2)$$

where:

$v_{MS_{\text{within}}}$: degrees of freedom of MS_{within}

The larger values of s_{bb} or U_{bb}^* were used as uncertainty contribution from the homogeneity, U_{bb} .

The results of the measurements are shown in Annex A (homogeneity study).

The results of evaluation are summarised in Table 2.

Table 2: Results of the homogeneity study for content of the elements in ERM-CZ120. Uncertainties are given as relative compared to the study average.

Elements	s_{bb}	U_{bb}^*	U_{bb}
	[%]	[%]	[%]
Arsenic	n.c.	0.8	0.8
Cadmium	1.1	0.6	1.1
Lead	n.c.	0.4	0.4
Nickel	0.2	0.4	0.4

n.c. = cannot be calculated as $MS_{\text{between}} < MS_{\text{within}}$

The potential between-unit variation is generally below 2 %. This material is therefore sufficiently homogeneous to be suitable as a reference material.

4.2 Minimum sample intake

The minimum sample intake is the minimum amount of sample that is representative for the whole unit. Samples equal or above the minimum sample intake guarantee the certified value within its stated uncertainty.

To estimate the minimum sample intake a series of measurements with decreasing amount of sample taken from three randomly selected vials was performed. The following sample intakes were tested: 50 mg, 40 mg, 30 mg, 20 mg, 10 mg and 5 mg. For each sample intake 6 samples were prepared. The samples were prepared and measured in the same way as in case of samples in the homogeneity study (see section 4.1).

The measurements were performed under repeatability conditions, and in a randomised manner to be able to separate a potential analytical drift from a trend related to the sample intake.

The results were not corrected for water content due to the same reasons as in case of the homogeneity study measurements (see section 4.1).

The minimum sample intake was established by comparison of variances obtained for 50 mg, 40 mg, 30 mg, 20 mg, 10 mg and 5 mg sample intakes with the variance obtained for results of the homogeneity study samples (150 mg sample intake). It was carried out using an F-test for equality of two sample variances with 5 degrees of freedom and a confidence level of 95 %.

The minimum sample intake is shown in the Table 3.

The individual values obtained during measurements related to the establishment of the minimum sample intake are shown in Annex B. The individual values obtained for sample intake 150 mg in the homogeneity study are shown in Annex A.

Table 3: Minimum sample intake

Element	Minimum sample intake [mg]
Arsenic	5
Cadmium	5
Lead	5
Nickel	5

Based on the results shown in Table 5 a minimum sample intake of 5 mg was established for all elements.

5. Stability

Stability testing is necessary to establish conditions for storage (long-term stability) as well as conditions for dispatch to the customers (short-term stability). During transport, especially in summer time, quite high temperatures can be reached. The stability studies were carried out using an isochronous design [6]. In that approach, samples are stored for a certain time at different temperature conditions. Afterwards, the samples are moved to conditions where further degradation can be assumed to be negligible ("reference conditions"). At the end of the isochronous storage the samples are analysed simultaneously under repeatability conditions. Analysis of the material (after various exposure times and temperatures) under repeatability conditions greatly improves the sensitivity of the stability tests. Time, temperature and light (UV-radiation) were regarded as the most relevant influences on stability of the material. The influence of UV-radiation was minimised by the choosing amber glass vials, which eliminate most of the incoming light. In addition, materials are stored and transported in the dark, thus practically eliminating the possibility of degradation by UV-radiation. Therefore, only the influences of time and temperature needed to be investigated.

5.1 Short-term stability study

The short-term stability samples were stored for 0, 1, 2 and 4 weeks at 18 °C and 60 °C. The reference temperature was -20 °C. Two samples per storage time were selected using a random stratified sampling scheme.

From each vial, three samples (about 150 mg sample intake) were prepared by digestion in a microwave oven using 5 ml HNO₃ and 0.2 ml HCl. The samples were analysed by means of inductively coupled plasma-sector field mass spectrometry (ICP-SFMS) with high (arsenic), medium (nickel) and low (cadmium, lead) mass resolution.

The measurements were performed under repeatability conditions, and in a randomised manner to be able to separate a potential analytical drift from a trend over storage time.

The results were not corrected for the water content due to the same reasons as in case of homogeneity samples (see section 4.1).

In the case of cadmium, the obtained results are lower than for other measurement data i.e. in case of cadmium in the long-term stability test. According to the explanation given by the laboratory, which carried out the measurements by means of ICP-SFMS (LR), the presence of tin, zircon and molybdenum at a relatively high level, has interfered with the measurement of the cadmium signal, which made a correction necessary. Most likely, the calculations carried out to correct for these interferences resulted in an over-correction of the signal and, consequently, in cadmium values that are too low. Since the measurements were performed under repeatability conditions and no analytical drift was found, they still can be used for the short-term stability assessment.

The results were screened for outlying values using a Grubbs-test. Some outlying individual results were found (see Table 4). As no technical reason for the outliers could be found all data were retained for statistical analysis.

The data points obtained were plotted against storage time at the test temperature and the regression line was calculated. The slope of the regression line was then tested for statistical significance. The results of the short-term stability study are shown in Table 4.

The short-term stability graphs are shown in the Annex C.

Table 4: Results of the short-term stability study for content of the elements in ERM-CZ120. Reference temperature - 20 °C

Element	Slope significant (95 % confidence)	u_{sts} [%/week]	Outliers
Test temperature: 18 °C			
Arsenic	no	0.3	none
Cadmium	no	0.5	none
Lead	no	0.6	none
Nickel	no	0.7	none
Test temperature: 60 °C			
Arsenic	no	0.3	none
Cadmium	no	0.5	2 ^a
Lead	no	0.6	none
Nickel	no	0.6	none

^a: on a 99 % confidence level

The uncertainties (u_{sts}) (Table 4) for the short-term stability study were between 0.3 % and 0.7 % for all compounds, therefore the potential degradation due to dispatch can be considered negligible and uncertainty contribution from the short-term stability is not included in the estimation of the total uncertainty of the material.

It was concluded that the material is stable at 18 °C and 60 °C for up to 4 weeks. The samples can be safely dispatched under conditions where the temperatures do not exceed 60 °C for up to 4 weeks, i.e. without cooling.

5.2 Long-term stability study

For the long-term stability study, samples were stored at 18 °C for 0, 4, 8, 12 months (1-year study). The reference temperature was set to -20 °C. Two samples per each storage time were selected using a random stratified sampling scheme.

From each vial, three samples (about 150 mg sample intake) were prepared by digestion in a microwave oven using 2 ml H₂O₂ and 8 ml HNO₃. The samples were analysed by means of ICP-QMS.

The measurements were performed under repeatability conditions, and in a randomised manner to be able to separate a potential analytical drift from a trend over storage time.

The results were not corrected for the water content due to the same reasons as in case of homogeneity samples (see section 4.1).

The results were screened for outlying values using a Grubbs-test. One outlying value for cadmium and one for nickel was found (see Table 5). As no technical reason for the outlier could be found all data were retained for statistical analysis.

The data points obtained were plotted against storage time at the test temperature and the regression line was calculated. The slope of the regression line was then tested for statistical significance. No significant slope was detected.

The long-term stability study results are shown in Table 5.

Table 5: Results of the evaluation of the 12 months long-term stability study for ERM-CZ120 at 18 °C. The given u_{ITS} is the projected estimate based on a 36 months shelf life. Uncertainties are given as relative compared to the study average.

Element	Outliers	Slope significant (95 % confidence)	u_{ITS} [%/36 months]
Arsenic	none	no	2.8
Cadmium	1 ^b	no	10.2
Lead	none	no	6.7
Nickel	1 ^a	no	3.0

^a: on a 95 % confidence level

^b: on a 99 % confidence level

Graphical representation of the long-term stability results are given in Annex D. The results show that the material is significantly stable at 18 °C. Uncertainties of stability during storage range from 2.8 to 10.2 % (based on a projected 36 months shelf-life). These uncertainties were taken up to the final uncertainties of the certified values. The shelf life will be revised, based on the results of the long-term stability study for 24 months isochronous storage and further stability monitoring.

6. Material characterisation

6.1 Approach

The material characterisation was based on a laboratory intercomparison approach, i.e. the content of selected elements in the material was determined in different laboratories that applied different measurement procedures to avoid method dependent bias.

Participants for the characterisation study were selected based on criteria that comprised both technical and quality management aspects. Fulfilment of the quality management requirements ensured the technical competence of the laboratory. Each participant was required to operate a quality system and to deliver documented evidence of its laboratory proficiency in the field of measurements of selected element in relevant matrices. Having an accreditation was not mandatory. However, when applicable the accreditation scope is stated in the list of participants.

The characterisation exercise started in December 2009 and finished in May 2010. Sixteen laboratories participated in this study.

The characterisation samples were selected using a random stratified sampling scheme and covered the whole batch.

Each laboratory received two vials of ERM-CZ120 and was requested to provide 6 independent results, 3 per vial.

The sample weighing had to be performed using conditions (i.e. temperature humidity and time) that are specified in the standard EN 12341. This means that before analysis, the sample had to be opened and kept for at least 48 h in the air-conditioned weighing room with a temperature of 20 °C ± 1 °C and a relative humidity of 50 % ± 5 % to reach equilibrium under weighing room conditions.

The sample preparations and measurements had to be spread over two days. That means that preparation of samples had to be performed during two separate days (three samples in one day and three in other day). Also the measurements had to be performed in two separate days (three samples in one day and three in other day).

As a control sample, the participants received a sample of SRM NIST 1648a "Urban Particulate Matter" to perform two analyses. The results were used only to support the evaluation of the characterisation results (if the QC sample result did not agree with the certified value, the result was rejected, see Section 6.3) and are therefore not reported here.

6.2 Methods used

A variety of acid digestion methods with different quantification steps (ICP-OES, ICP-QMS, ICP-SFMS) as well as a non-destructive method (k_0 -NAA) were used to characterise the material.

All methods used during the characterisation study are summarised in Annex E. The lab code consists of a number assigned to each laboratory and abbreviation of the measurement method used (e.g. L01/ICP-OES).

6.3 Evaluation of results

The characterisation campaign resulted in 6 to 7 datasets per element. All individual results of the participants, grouped per element are shown in tabular and graphical form in Annex F.

The obtained data were first checked for compliance with the requested analysis protocol and for their validity based on technical reasons. The following criteria were considered during the evaluation:

- compliance with the analysis protocol: weighing conditions, sample preparations and measurements performed on two days, order of analysis;
- absence of 'less than' values,
- measurement RSD for single dataset: acceptance value was $\leq 10\%$,
- if the QC sample result did not agree with the certified value, the result was rejected,
- method performance, i.e. delivery of incorrect results for more than half of the analysed elements within one quantification method clearly indicates that the method is not under control. This was verified with the QC sample. A result is considered incorrect when the combined standard uncertainty of the measurement of the QC sample and of the certified value does not cover the difference between the certified value and the measurement result (see also ERM Application Note 1, www.erm-crm.org [8]).

Based on the above some datasets were rejected as not technically valid (see Table 6).

Table 6: Datasets that shown non-compliances with the analysis protocol and technical specifications, and action taken

Lab/method code	Element	Description of problem	Action taken
L02/ICP-QMS	All	Weighing was not performed according to the standard EN12341	Results rejected as not technically valid
L03/ICP-SFMS	All	Weighing was not performed according to the standard EN12341	Results rejected as not technically valid
L04/ICP-QMS	All	Incorrect results for all analysed elements in the QC sample	Results rejected as not technically valid
L06/ICP-QMS	All	Weighing was not performed according to the standard EN12341	Results rejected as not technically valid
L07/ICP-QMS	All	Weighing was not performed according to the standard EN12341	Results rejected as not technically valid
L09/ICP-OES	As	RSD 11%	Results rejected as not technically valid
L10/FAAS-vapour system	As	Incorrect results for As in the QC sample	Results rejected as not technically valid
L10/FAAS	Cd, Ni, Pb	RSD 37 %, 23 % and 22 %, respectively	Results rejected as not technically valid
L12/ k_0 -NAA	Cd	Lab reported 'less than' values	Results rejected as not technically valid
L15/HAFS	As	RSD 11%	Results rejected as not technically valid

The datasets accepted on technical grounds were tested for normality of the distribution of the laboratory means using the "Skewness and Kurtosis" statistical test. All data were normally distributed.

Then they were tested for outlying laboratories using Dixon, Grubbs and Nalimov t-test. Their mean cadmium value from Laboratory 11 was identified as outlier. No technical reason was found for excluding this value and, considering the associated measurement uncertainty reported by the concerned laboratory, the mean value is not significantly different from the certified value. Therefore, the result was retained for the calculation of the mean and uncertainty of characterization value (u_{char}).

The characterization value was calculated as mean of means of all accepted datasets. The contribution of the material characterisation to the uncertainty of the certified value u_{char} was estimated as the standard error of the mean of means, and was calculated as the relative standard deviation divided by the square root of the number of accepted datasets. The resulting data are summarised in Table 7.

The results of characterisation study are shown in the Annex F.

Table 7: Summary of the characterisation study of ERM-CZ120. Uncertainties are given as relative compared to the study average.

Element	Number of independent, valid datasets	Mean of laboratory means [mg/kg]	u_{char} [%]
Arsenic	6	7.1	3.4
Cadmium	7	0.90	6.6
Lead	7	113	3.1
Nickel	7	58	4.5

7. Assigned values

7.1 Certified values and their uncertainties

The unweighted mean of means of the accepted datasets as shown in Table 8 was assigned as a certified value for the selected elements.

The certified uncertainty consists of uncertainties related to characterisation, $u_{char,rel}$ (see Section 6.3), between-bottle heterogeneity, $u_{bb,rel}$ (see Section 4.1) and degradation during long-term storage, $u_{lts,rel}$ (see Section 5.2). These different contributions were combined to estimate the expanded, relative uncertainty of the certified value ($U_{CRM,rel}$) as given by:

$$U_{CRM,rel} = k \cdot \sqrt{u_{char,rel}^2 + u_{bb,rel}^2 + u_{lts,rel}^2} \quad (3)$$

where:

k : coverage factor equal to 2, representing a level of confidence of about 95 %.

The certified values and their uncertainties are summarised in Table 10.

Table 8: Certified values and their uncertainties for ERM-CZ120

Element	Certified value [mg/kg]	$u_{char,rel}$ [%]	$u_{bb,rel}$ [%]	$u_{lts,rel}$ [%]	$U_{CRM,rel}$ [%]	U_{CRM} [mg/kg]
Arsenic	7.1	3.4	0.8	2.8	8.8	0.7
Cadmium	0.90	6.6	1.1	10.2	24.4	0.22
Lead	113	3.1	0.4	6.7	14.7	17
Nickel	58	4.5	0.4	3.0	10.9	7

7.2 Additional material information

Data has been provided by two laboratories, each delivering results of six replicate measurements using k_0 -NAA (Annex G).

In case of the total carbon, total organic carbon, elemental carbon and silicon the mass fractions represent the mean values of three individual results provided by one laboratory.

The total carbon and the total organic carbon were determined by coulometric titration and the elemental carbon was determined by use of the high temperature combustion and coulometric detection according to VDI 2465 Blatt 1 [7]. Silicon was determined by using X-ray fluorescence spectrometry (XRF).

The additional material information is summarised in Table 9. Additionally, in the Annex G, the individual values for each element are given.

Table 9: Additional material information

Element	Mass fraction Value [mg/kg]	Element	Mass fraction Value [mg/kg]
Aluminium	34100 ¹⁾	Molybdenum	33.2 ²⁾
Antimony	64.7 ²⁾	Neodymium	22.2 ¹⁾
Barium	562.2 ²⁾	Potassium	10998 ²⁾
Bromine	10.2 ²⁾	Rubidium	52.3 ²⁾
Caesium	3.1 ²⁾	Samarium	4.1 ²⁾
Calcium	63043 ²⁾	Scandium	7.4 ²⁾
Cerium	56.8 ²⁾	Silicon	229000 ⁴⁾
Chlorine	10033 ¹⁾	Sodium	14211 ²⁾
Chromium	201 ²⁾	Strontium	251 ²⁾
Cobalt	14.3 ²⁾	Tantalum	1.0 ²⁾
Copper	462 ¹⁾	Terbium	0.6 ²⁾
Dysprosium	3.3 ¹⁾	Thorium	7.0 ²⁾
Elemental carbon	45433 ³⁾	Titanium	4372 ¹⁾
Europium	0.8 ²⁾	Total carbon	111333 ³⁾
Gallium	8.7 ¹⁾	Total organic carbon	76633 ³⁾
Gold	0.02 ¹⁾	Tungsten	4.1 ¹⁾
Hafnium	8.4 ²⁾	Uranium	2.6 ²⁾
Iron	38144 ²⁾	Vanadium	72.4 ¹⁾
Lanthanum	25.0 ²⁾	Ytterbium	1.7 ²⁾
Magnesium	13200 ¹⁾	Zinc	1240 ²⁾
Manganese	611 ¹⁾	Zirconium	341 ²⁾

¹⁾ The mass fraction represents the mean value of two results provided by two laboratories. The measurements were performed by k₀-NAA.

²⁾ The mass fraction represents the mean value of six individual results provided by one laboratory. The measurements were performed by k₀-NAA.

³⁾ The mass fraction represents the mean value of three individual results provided by one laboratory. The results were obtained by coulometric titration.

⁴⁾ The mass fraction represents the mean value of three individual results provided by one laboratory. The results were obtained by X-ray fluorescence spectroscopy.

8. Metrological traceability and commutability

8.1 Metrological traceability

Traceability of the certified values to the SI is ensured through the set-up of the characterisation. The participating laboratories used a number of different methods for the sample preparation and different methods for the final determination, thus eliminating any possibility of method dependent results. In addition, different calibrants were used, including commercial standard solutions and CRMs. Traceability of the individual results was demonstrated by the fact that most laboratories also used matrix CRMs for quality control (see Annex E).

8.2 Commutability

Commutable CRMs should exhibit a similar analytical behaviour for given methods as a real laboratory sample. The CRM was prepared for laboratories performing air quality measurements. The most of laboratories participating in the characterisation belong to the group of National Air Quality Reference Laboratories (AQUILA), which use the preparation methods and the determination methods according to the standards EN 12341 and EN 14902. However, a few laboratories prepared the samples using in-house developed methods of sample preparation. The good agreement between the results obtained according to different methods of sample preparation indicates commutability of the material.

Commutability of the material is also confirmed by the results of the feasibility study performed before production and certification of the material. The study was performed in cooperation with voluntary laboratories of the AQUILA group. The evaluation of the results has shown that the tunnel dust was suitable as a PM₁₀ material in terms of the analytes content and material handling.

9. Instructions for use

9.1 Storage conditions

The material shall be stored at 18 °C ± 5 °C in the darkness. However, the European Commission cannot be held responsible for changes that happen during storage of the material at the customer's premises, especially of opened samples.

9.2 Safety and protection for the environment

The usual laboratory safety measures apply. As the material consists of fine particles, appropriate protection against inhalation is recommended.

9.3 Use of the material

The vials shall be shaken by turning upside down for at least 2 min before opening to ensure the material re-homogenisation. The sample weighing shall be performed using conditions (i.e. temperature humidity and time) that are specified in the standard EN 12341. It means that before analysis, the sample has to be opened and kept for at least 48 h in the air-conditioned weighing room with a temperature of 20 °C ± 1 °C and a relative humidity of 50 % ± 5 % to reach equilibrium under weighing room conditions.

9.4 Minimum sample intake

The minimum sample intake representative for all elements is 5 mg.

9.5 Use of the certified value

The main purpose of the material is to assess method performance, i.e. for checking accuracy of analytical results. As any reference material, it can also be used for control charts or validation studies.

Comparing an analytical result with the certified value

A result is unbiased if the combined standard uncertainty of measurement and certified value covers the difference between the certified value and the measurement result (see also ERM Application Note 1), www.erm-crm.org [8].

Use as a calibrant

It is not recommended to use matrix materials as calibrants. If used nevertheless, the uncertainty of the certified value shall be taken into account in the estimation of the measurement uncertainty.

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Annexes

Annex A: Results of the homogeneity study, ERM-CZ120

Annex B: Results of the minimum sample intake study, ERM-CZ120

Annex C: Results of the short-term stability study, ERM-CZ120

Annex D: Results of the long-term stability study, ERM-CZ120

Annex E: Characterisation study – laboratories and methods, ERM-CZ120

Annex F: Characterisation study – results, ERM-CZ120

Annex G: Additional material information, ERM-CZ120

Annex A: Results of the homogeneity study, ERM-CZ120**Arsenic**

Bottle number	Sequence number	Result [mg/kg]	Sequence number	Result, [mg/kg]	Sequence number	Result [mg/kg]
81	15	6.636	33	6.574	43	6.629
202	1	6.468	35	6.508	49	6.652
290	5	6.416	26	6.721	48	6.351
349	3	6.491	27	6.644	53	6.698
554	7	6.422	25	6.843	44	6.742
605	2	6.693	20	6.764	54	6.688
748	10	6.482	24	6.523	37	6.507
897	17	6.424	19	6.419	50	6.582
973	9	6.466	22	6.794	51	6.592
1085	14	6.229	28	6.731	52	6.784
1241	16	6.425	30	6.492	45	6.429
1324	13	6.409	36	7.080	47	6.733
1398	8	6.226	34	6.502	46	6.697
1559	12	6.522	31	6.693	42	6.922
1801	6	6.108	29	6.590	39	6.451
1874	18	6.419	32	6.593	41	6.728
1926	11	6.571	23	6.464	40	6.516
2121	4	6.429	21	6.600	38	6.802

Cadmium

Bottle number	Sequence number	Result [mg/kg]	Sequence number	Result [mg/kg]	Sequence number	Result [mg/kg]
81	15	0.9510	33	0.9420	43	0.9055
202	1	0.8794	35	0.9350	49	0.9466
290	5	0.9351	26	0.9781	48	0.9441
349	3	0.9493	27	0.9258	53	0.9596
554	7	0.9854	25	0.9686	44	0.9745
605	2	0.9528	20	0.9525	54	0.9295
748	10	0.9226	24	0.9342	37	0.9311
897	17	0.9172	19	0.9794	50	0.9537
973	9	0.9824	22	0.9473	51	0.9443
1085	14	0.9563	28	0.9734	52	0.9644
1241	16	0.9440	30	0.9354	45	0.9294
1324	13	0.9462	36	0.9677	47	0.9496
1398	8	0.9402	34	0.9691	46	0.9946
1559	12	0.9152	31	0.9295	42	0.9529
1801	6	0.9312	29	0.9491	39	0.9476
1874	18	0.9750	32	0.9740	41	0.9144
1926	11	0.9109	23	0.9599	40	0.9078
2121	4	0.9042	21	0.9233	38	0.9374

Annex A: Results of the homogeneity study, ERM-CZ120**Nickel**

Bottle number	Sequence number	Result [mg/kg]	Sequence number	Result [mg/kg]	Sequence number	Result [mg/kg]
81	15	56.27	33	56.00	43	54.39
202	1	55.20	35	56.05	49	57.35
290	5	55.38	26	56.89	48	54.84
349	3	56.29	27	55.93	53	56.26
554	7	57.48	25	57.26	44	56.39
605	2	56.29	20	56.98	54	57.7
748	10	56.75	24	55.75	37	55.48
897	17	54.53	19	54.99	50	56.91
973	9	57.09	22	56.34	51	55.46
1085	14	54.55	28	57.99	52	55.96
1241	16	55.96	30	56.07	45	55.19
1324	13	56.86	36	56.87	47	57.2
1398	8	55.52	34	56.86	46	55.47
1559	12	55.16	31	57.42	42	56.05
1801	6	56.36	29	55.81	39	56.6
1874	18	56.21	32	57.11	41	55.23
1926	11	56.99	23	57.44	40	56.23
2121	4	55.00	21	55.72	38	55.74

Lead

Bottle number	Sequence number	Result [mg/kg]	Sequence number	Result [mg/kg]	Sequence number	Result [mg/kg]
81	15	110.2	33	111.0	43	108.1
202	1	108.1	35	110.5	49	112.0
290	5	110.6	26	111.7	48	107.9
349	3	110.5	27	112.8	53	111.4
554	7	112.8	25	111.7	44	110.4
605	2	111.7	20	111.6	54	111.0
748	10	112.1	24	108.5	37	108.2
897	17	108.1	19	108.9	50	111.2
973	9	111.7	22	108.9	51	109.5
1085	14	107.5	28	111.9	52	110.5
1241	16	111.0	30	111.5	45	109.7
1324	13	110.4	36	111.1	47	111.9
1398	8	107.1	34	111.5	46	110.4
1559	12	111.5	31	113.0	42	109.8
1801	6	109.5	29	110.6	39	108.8
1874	18	111.0	32	112.9	41	109.4
1926	11	111.7	23	112.0	40	110.9
2121	4	109.9	21	107.8	38	109.2

Annex B: Results of the minimum sample intake study, ERM-CZ120

Arsenic

150 mg Homogeneity study results	Replicate #	50 mg		40 mg		30 mg		20 mg		10 mg		5 mg	
		Bottle number	Result [mg/kg]	Bottle number	Result [mg/kg]	Bottle number	Result [mg/kg]	Bottle number	Result [mg/kg]	Bottle number	Result [mg/kg]	Bottle number	Result [mg/kg]
Results in Annex A	1	2095	6.681	2095	6.909	34	6.821	999	6.749	999	6.785	999	7.182
	2	34	6.890	34	6.872	2095	6.990	999	6.908	999	6.880	999	6.510
	3	34	6.975	34	6.919	34	6.700	999	6.874	999	6.768	999	6.689
	4	2095	7.017	34	7.003	2095	6.970	999	6.725	999	6.630	999	6.549
	5	34	7.058	2095	6.724	2095	6.633	999	7.016	999	6.501	999	6.866
	6	2095	7.150	2095	7.053	2095	6.911	999	6.940	999	7.043	999	6.672

Cadmium

150 mg Homogeneity study results	Replicate #	50 mg		40 mg		30 mg		20 mg		10 mg		5 mg	
		Bottle number	Result [mg/kg]	Bottle number	Result [mg/kg]	Bottle number	Result [mg/kg]	Bottle number	Result [mg/kg]	Bottle number	Result [mg/kg]	Bottle number	Result [mg/kg]
Results in Annex A	1	2095	0.8667	2095	0.8995	34	0.8772	999	1.044	999	1.012	999	1.049
	2	34	0.8686	34	0.8609	2095	0.9188	999	0.957	999	1.132	999	0.924
	3	34	0.9037	34	0.8421	34	0.878	999	1.004	999	1.035	999	1.140
	4	2095	0.9403	34	0.9048	2095	0.9133	999	1.019	999	1.065	999	0.962
	5	34	0.8682	2095	0.888	2095	0.8828	999	1.023	999	1.059	999	1.008
	6	2095	0.9426	2095	0.8201	2095	0.8984	999	1.048	999	0.951	999	0.879

Annex B: Results of the minimum sample intake study, ERM-CZ120

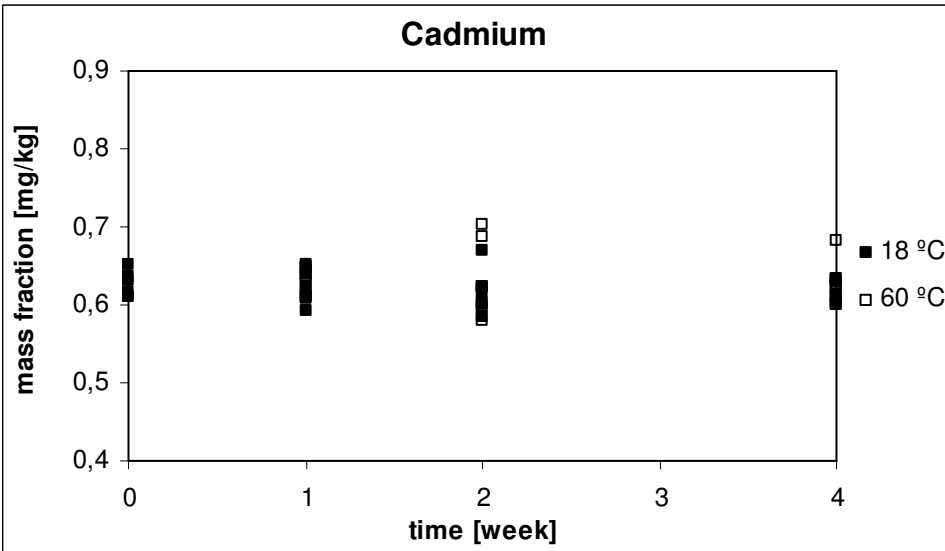
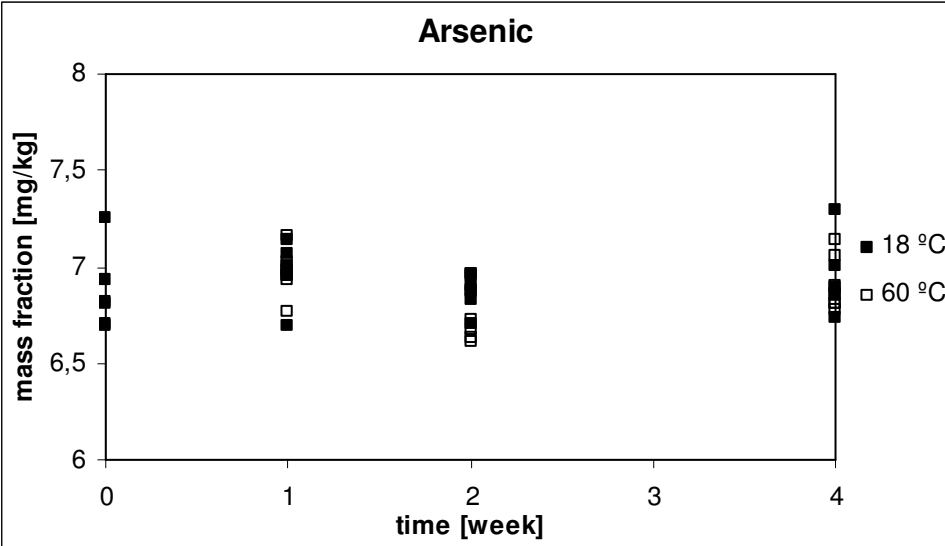
Nickel

150 mg Homogeneity study results	Replicate #	50 mg		40 mg		30 mg		20 mg		10 mg		5 mg	
		Bottle number	Results [mg/kg]	Bottle number	Results [mg/kg]	Bottle number	Results [mg/kg]	Bottle number	Results [mg/kg]	Bottle number	Results [mg/kg]	Bottle number	Results [mg/kg]
Results in Annex A	1	2095	51.69	2095	52.12	34	53.94	999	54.28	999	55.66	999	57.97
	2	34	51.37	34	52.33	2095	57.48	999	53.85	999	56.05	999	51.85
	3	34	52.72	34	52.45	34	52.88	999	53.96	999	52.39	999	53.53
	4	2095	53.27	34	53.17	2095	53.82	999	53.55	999	53.84	999	50.50
	5	34	52.41	2095	53.64	2095	51.56	999	52.61	999	52.06	999	56.45
	6	2095	53.68	2095	52.42	2095	54.31	999	53.29	999	53.40	999	51.71

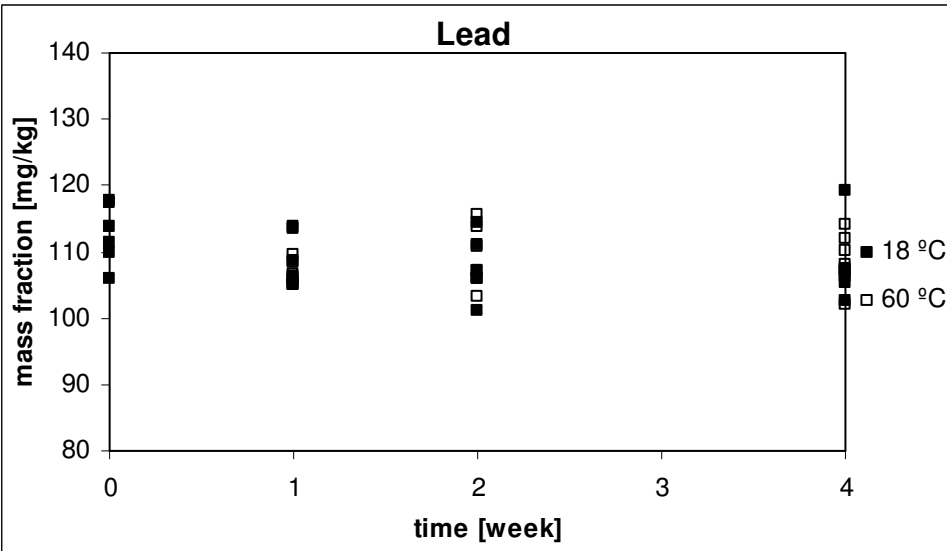
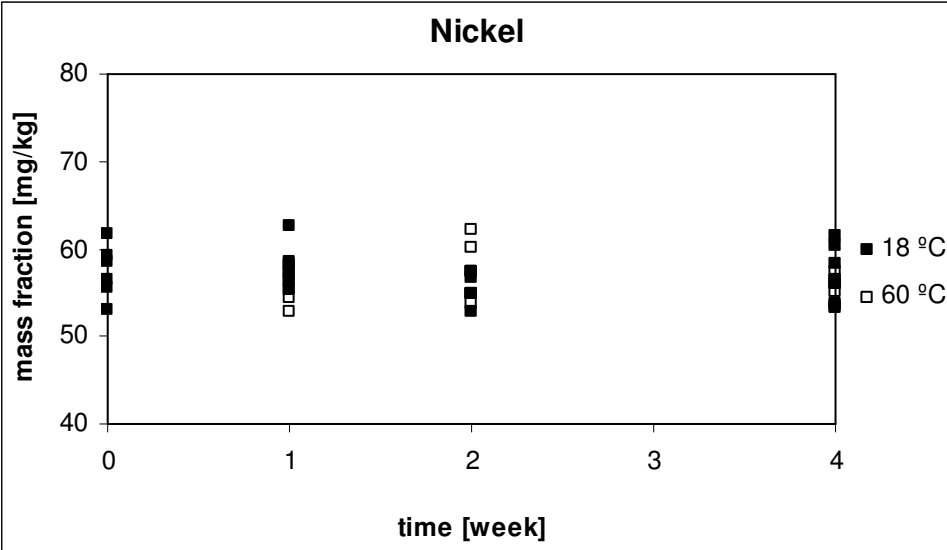
Lead

150 mg Homogeneity study results	Replicate #	50 mg		40 mg		30 mg		20 mg		10 mg		5 mg	
		Bottle number	Results [mg/kg]	Bottle number	Results [mg/kg]	Bottle number	Results [mg/kg]	Bottle number	Results [mg/kg]	Bottle number	Results [mg/kg]	Bottle number	Results [mg/kg]
Results in Annex A	1	2095	109.5	2095	109.8	34	113.1	999	114.0	999	113.6	999	119.5
	2	34	111.9	34	114.6	2095	113.6	999	115.2	999	111.3	999	114.0
	3	34	112.7	34	112.6	34	112.7	999	115.6	999	112.7	999	114.1
	4	2095	112.5	34	112.7	2095	113.5	999	117.2	999	114.2	999	103.2
	5	34	112.6	2095	112.4	2095	110.3	999	112.9	999	115.4	999	115.9
	6	2095	115.8	2095	112.1	2095	114.0	999	114.3	999	114.6	999	109.2

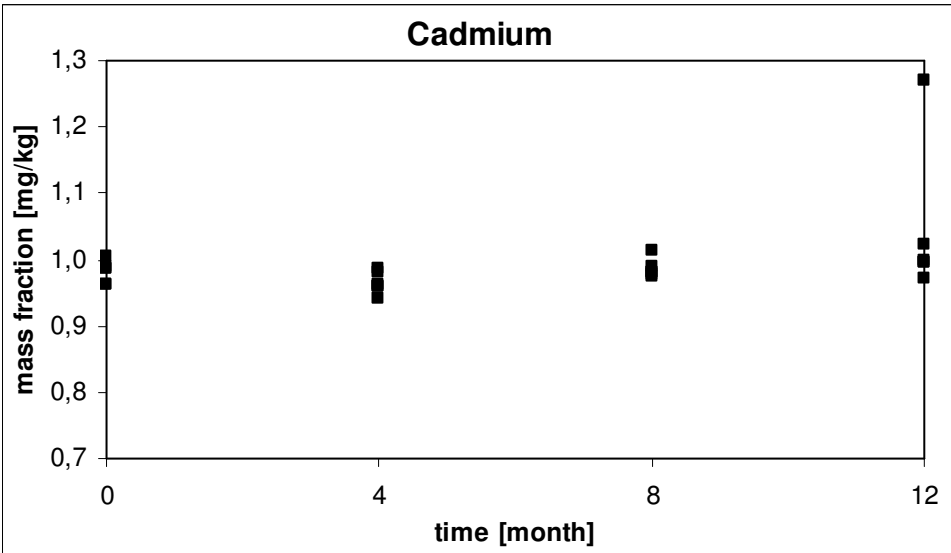
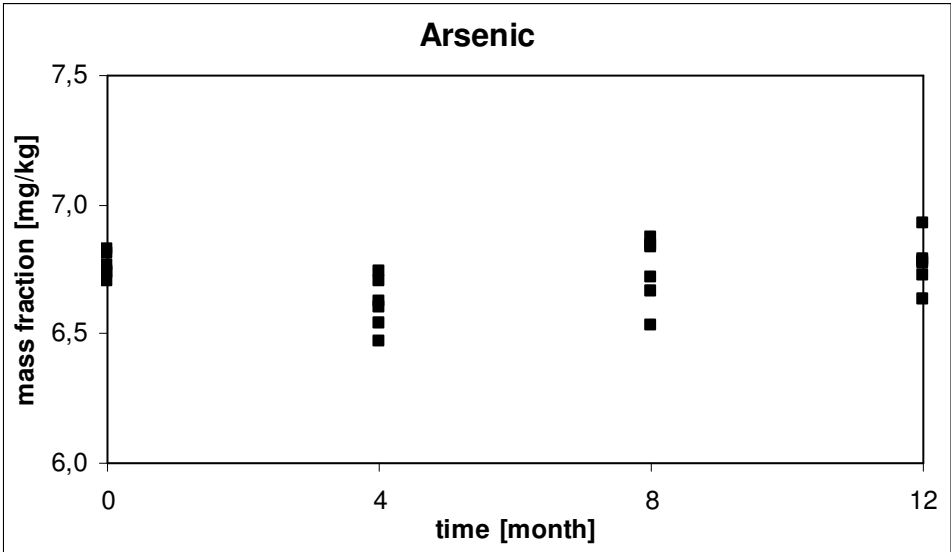
Annex C: Results of the short-term stability study, ERM-CZ120



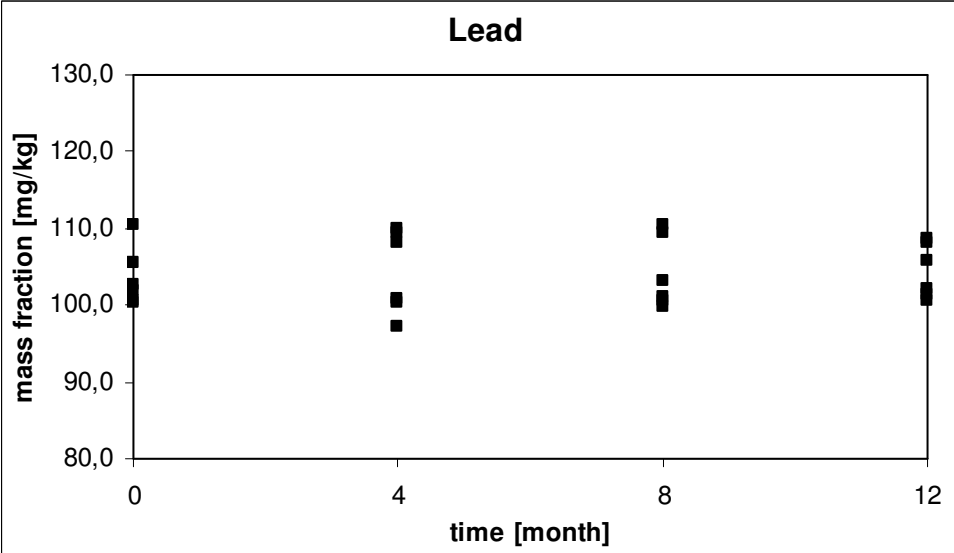
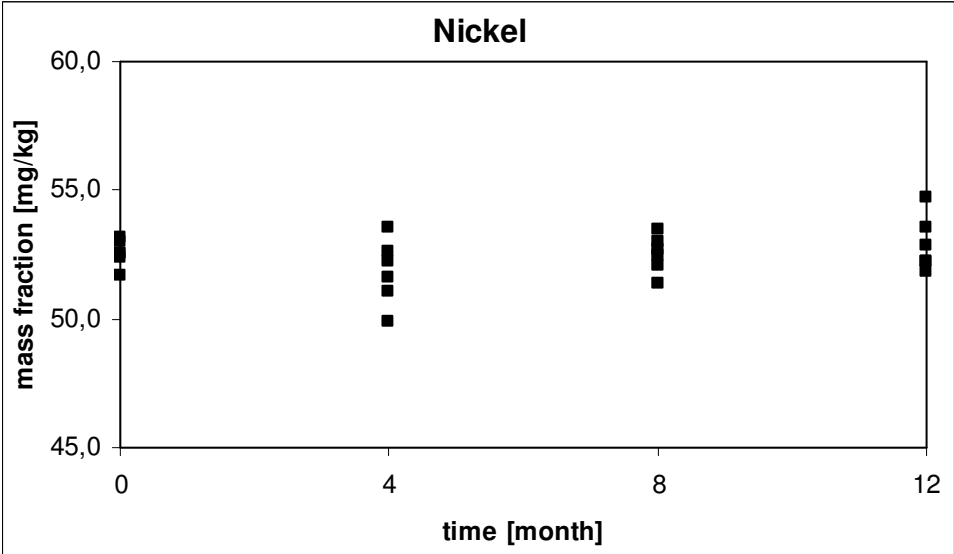
Annex C: Results of the short-term stability study, ERM-CZ120



Annex D: Results of the long-term stability study, ERM-CZ120



Annex D: Results of the long-term stability study, ERM-CZ120



Annex E: Characterisation study – laboratories and methods, ERM-CZ120

Lab code/Method	Element	Sample mass [g]	Sample preparation	Calibrants	Instrumentation and measurement method
L01/k ₀ -NAA	As	0.067 – 0.081	No preparation	Au (IRMM-530) flux monitor QC: NIST SRM 1633b coal fly ash	25209 min irradiation with flux 3.00×10^{11} neutrons/(cm ² s) Decay time: 1.1day Measuring time: 48h Isotope used: As-76 Gamma line used: 559 keV
L02/ICP-QMS	All	0.04746 – 0.06234	Microwave digestion was performed using Milestone Ethos 1 with temperature controlled closed vessel. For digestion 8 ml HNO ₃ and 2 ml H ₂ O ₂ were used The digestion was performed within 60 min: with max temperature 220 °C and max pressure 55 bar.	Multi-element standard Perkin Elmer QC: NIST SRM 1648a	Equipment: ICP-QMS (Perkin Elmer, Elan 6100), Calibration: seven-point external calibration, Isotopes monitored: ⁷⁵ As, ¹¹¹ Cd, ⁶² Ni, ²⁰⁶⁺²⁰⁷⁺²⁰⁸ Pb, Internal standards: Ge, Rh
L03/ICP-SFMS	All	0.00421 – 0.00811	Teflon coated block digestion system Digiprep MS with temperature programme - ramp to 103 °C in 40 min., 120 min. at 103 °C was used for digestion of the samples. The samples were digested with 4 ml of H ₂ O ₂ and 16 ml of HNO ₃ in a digestion vessel (DigiTUBE) with a glass ball condenser.	ISB-CAL-356-REV1, ISB-CAL-356-REV2, ISB-CAL-356-REV3, ISB-CAL-356-REV4 produced by CPI QC: NIST SRM 1648a	Equipment: ICP-SFMS (ThermoFisher Scientific, Element2), Calibration: five-point external calibration, Isotopes monitored: ⁷⁵ As (HR), ¹¹¹ Cd (LR), ⁶⁰ Ni (MR), ²⁰⁶⁺²⁰⁷⁺²⁰⁸ Pb (LR), Internal standards: Re, Rh, Ge
L04/ICP-QMS	As, Cd	0.0989 – 0.1198	Microwave digestion was performed using Microwave MARS, CEM. For digestion 5 ml HNO ₃ and 1 ml H ₂ O ₂ were used. The digestion was performed within 25 min: with max temperature 200 °C and max pressure 28 bar.	Environmental Calibration Standard, Agilent Technologies	Equipment: ICP-QMS (ICP-MS Agilent Technologies 7500ce with collision cell), Calibration: four-point external calibration, Isotopes monitored: ⁷⁵ As, ¹¹¹ Cd, Internal standards: Ge, In
L04/ICP-OES	Ni, Pb			QCS-26 High Purity Standard	Equipment: ICP-OES (ICP-OES Vista-MPX Varian), Calibration: five-point external calibration, Wavelengths [nm]: 231.604 (Ni), 220.353(Pb),
L05/ICP-QMS	All	0.1437 – 0.1541	Microwave digestion was performed using Microwave MARS, CEM. For digestion 8 ml HNO ₃ and 2 ml H ₂ O ₂ were used. The digestion was performed within 45 min: with max temperature 220 °C and max pressure 45 bar.	Multielemental calibration solutions prepared from monoelemental standard solutions produced by NIST	Equipment: ICP-QMS (PerkinElmer Elan DRC II), Calibration: six-point external calibration, Isotopes monitored: ⁷⁵ As, ¹¹¹ Cd, ⁶⁰ Ni, ²⁰⁸ Pb, Internal standards: None

Annex E: Characterisation study – laboratories and methods, ERM-CZ120

L06/GFAAS	As			Multielements Standard CPI	Calibration: five-point external calibration, Wavelengths [nm]: 193.7 Slit width [nm]: 0.2
L06/ICP-QMS	Cd	0.05797 – 0.0746	Microwave digestion was performed using Microwave MARS Xpress, CEM. The digestion was performed within 20 min: with max temperature 180 °C.	Multielements Standard SCP Science	Calibration: six-point internal calibration, Isotopes monitored: ¹¹¹ Cd, Internal standards: Tb
L06/ICP-OES	Ni, Pb			Multielements Standard Techlab	Calibration: five-point external calibration, Wavelengths [nm]: 231.604 (Ni), 220.353(Pb),
L07/ICP-QMS	All	0.0274 – 0.0342	Microwave digestion was performed using a closed system. For digestion 8 ml HNO ₃ and 2 ml H ₂ O ₂ were used. The digestion was performed within 35 min: with max temperature 220 °C and max pressure 18 bar.	Multi-mix 10 ppm, Inorganic Ventures	Equipment: ICP-QMS (Varian 820-MS), Calibration: six-point internal calibration, Isotopes monitored: ⁷⁵ As, ¹¹¹ Cd, ⁶⁰ Ni, ²⁰⁸ Pb, Internal standards: In, Y
L8/ICP-OES	Cd, Ni, Pb	0.13936 – 0.16698	Microwave digestion was performed using Microwave MARS 5, CEM. For digestion 4 ml of HNO ₃ , 3 ml of H ₂ O ₂ and 10 ml of H ₂ O were used. The digestion was performed within 83 min: with max temperature 180 °C and max pressure 120 bar.	ICP Multi Element Standard Solution IV CertiPUR Merck	Equipment: ICP-OES (VARIAN ICP Liberty Series II Axial), Calibration: seven-point external calibration, Wavelengths [nm]: 228.082 (Cd), 231.604 (Ni), 220.353(Pb),
L9/ICP-OES	All	0.0499 – 0.0518	Microwave digestion was performed using Microwave MARS 5, CEM. For digestion 10 ml of HNO ₃ were used. The digestion was performed within 30 min: with max temperature 200 °C.	Merck 119773, Merck ICP-IV, 111355 QC: NIST SRM 1648a	Equipment: ICP-OES (VARIAN ICP Liberty Series II Axial), Calibration: three-point external calibration, Wavelengths [nm]: 188.979 (As), 228.082 (Cd), 231.604 (Ni), 220.353(Pb),
L010/FAAS-vapour-system	As	0.05		Arsenic standard for ICP, Fluka	Equipment: FAAS (Perkin Elmer) with vapour system, Calibration: five-point external calibration, Wavelengths [nm]: 193.7 9 (As), 228.8 (Cd), 232 (Ni), 217 (Pb),
L10/FAAS	Cd, Ni, Pb		Microwave digestion was performed using MW-Etnos-Plus, Italy. The digestion was performed within 25 min: with max temperature 180 °C and max pressure 600 bar.	Multielement standard solution V for ICP, Fluka	

Annex E: Characterisation study – laboratories and methods, ERM-CZ120

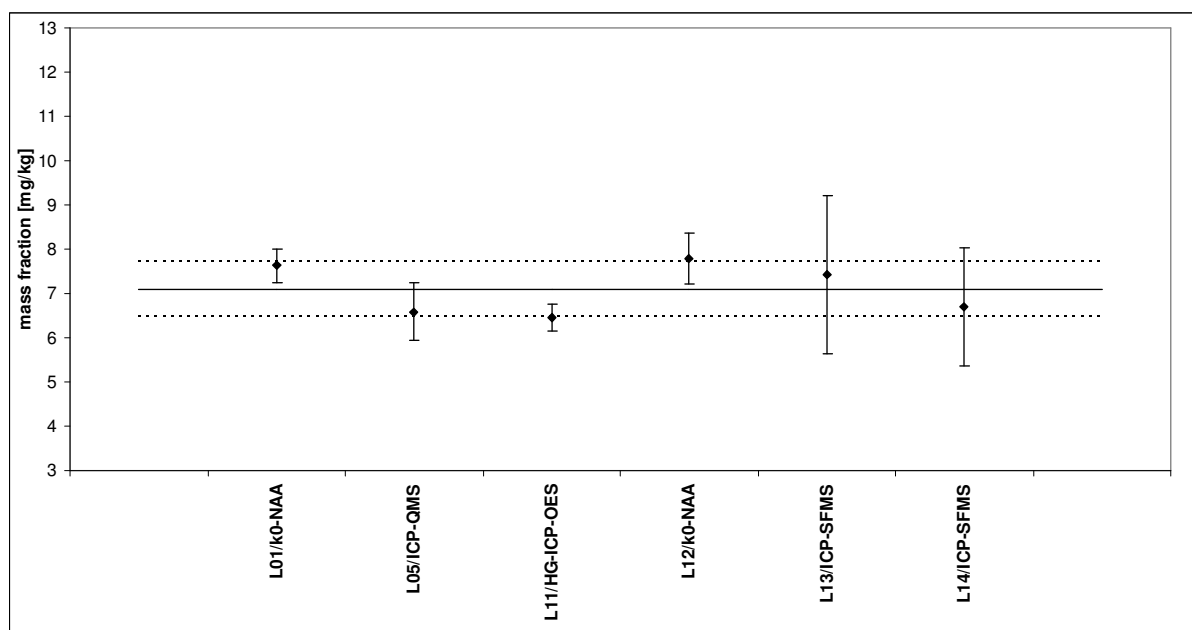
L11/HG-ICP-AES	As	0.0953 – 0.1027	Microwave digestion was performed using Anton Paar, Multiwave 3000. For digestion HNO ₃ , HCl, HF and H ₂ BO ₄ were used. The digestion was performed within 50 min: with max temperature 240 °C and max pressure 60 bar	Certified single standard, CPI	Equipment: HG-ICP-OES (Optima 7300, Perkin Elmer, with a HG unit as sample introduction system, mixing (1:1) the sample on-line with NaBH ₄ (1%)/NaOH (0.3%) in the HG reaction block (Perkin Elmer). Calibration: three-point external calibration Wavelengths [nm]: 188.979 (As)
L11/ICP-OES	Cd, Ni, Pb			Certified single standard, CPI and SCP Science	Equipment: ICP-OES (Optima 7300, Perkin Elmer) Calibration: five-point external calibration, Wavelengths [nm]: 228.082 (Cd), 231.604 (Ni), 220.353(Pb),
L12/k ₀ -NAA	As, Cd	0.0512 – 0.0539	No preparation	Al-Au(0.1%), IRMM-530RA QC: BCR-320R Channel Sediment	840 min irradiation with flux 1.1 x 10 ¹² neutrons/(cm ² s) Decay time: 3-11 days Measuring time: 5800 s Isotope used: As-76, In115m, Gamma line used: 559 keV, 336.2 keV
L13/ICP-SFMS	All	0.099451 – 0.101967	Microwave digestion was performed using Milestone Mega MLS 1200. For digestion HNO ₃ , HCl and HF were used.	Multi element standard, SPEX	Equipment: ICP-SFMS Calibration: external calibration, Isotopes monitored: ⁷⁵ As, ¹¹¹ Cd, ⁶⁰ Ni, ²⁰⁸ Pb, Internal standards: Rh
L14/ICP-SFMS	As	0.03154 – 0.0435	Microwave digestion was performed using Anton Parr Multiwave. For digestion 4 ml of HNO ₃ were used The digestion was performed within 30 min: with max temperature 200 °C and max pressure 70 bar.	VWR BDH Prolabo, BDH Aristar	Equipment: ICP-SFMS (Thermo Axiom) Calibration: seven-point internal calibration, Isotopes monitored: ⁷⁵ As, Internal standards: Ga, Rh
L14/ICP-QMS	Cd, Ni, Pb				Equipment: ICP-QMS (Perkin Elmer Elan 6000 (Cd, Pb), Agilent 7500ce ICPMS (Ni)) Calibration: seven-point internal calibration, Isotopes monitored: ¹¹¹ Cd, ⁶⁰ Ni, ²⁰⁸ Pb, Internal standards: Rh
L15/HG AFS	As	0.07217 – 0.08953	Microwave digestion was performed using Berghof DAB-3. For digestion 3.8 ml of HNO ₃ and 0.2 ml HF were used. The digestion was performed within 600 min: with max temperature 190°C.	Inorganic Venture QC: BCR 038 + NBS1633B	Equipment: HG AFS Calibration: four-point external calibration, Wavelengths [nm]: 188.979 (As)
L15/ICP-AES	Cd, Ni, Pb				Equipment: ICP-AES (Varian Vista AX CCD simultaneous ICP-AES) Calibration: four-point external calibration, Wavelengths [nm]: 214.439 (Cd), 231.604 (Ni), 220.353(Pb)
L16	Due to technical problems laboratory could not deliver the results				

Arsenic

Lab code/Method	Individual results ^a [mg/kg]						Mean value [mg/kg]	s [mg/kg]	U_{Lab} [mg/kg]
L01/k0-NAA	7.60	7.63	7.45	7.57	7.71	7.79	7.63	0.12	0.39
L05/ICP-QMS	6.79	6.74	6.45	6.65	6.51	6.37	6.59	0.17	0.66
L11/HG-ICP-OES	6.35	6.39	6.53	6.46	6.56	6.39	6.45	0.08	0.30
L12/k0-NAA	7.97	7.23	7.68	7.98	7.73	8.09	7.78	0.31	0.58
L13/ICP-SFMS	8.031	6.997	7.601	6.716	7.315	7.891	7.425	0.513	1.797
L14/ICP-SFMS	6.783	7.228	6.265	6.513	6.718	6.652	6.693	0.320	1.339

^a: values reported on mass of the sample after conditioning the sample using conditions as described in EN12341

Error bars in the graph represent expanded uncertainties (U_{Lab}) as reported by the participating laboratories. Solid line represents the certified value. Broken lines represent the expanded uncertainty of the certified value.



Excluded results were not used for the calculation of the certified value.

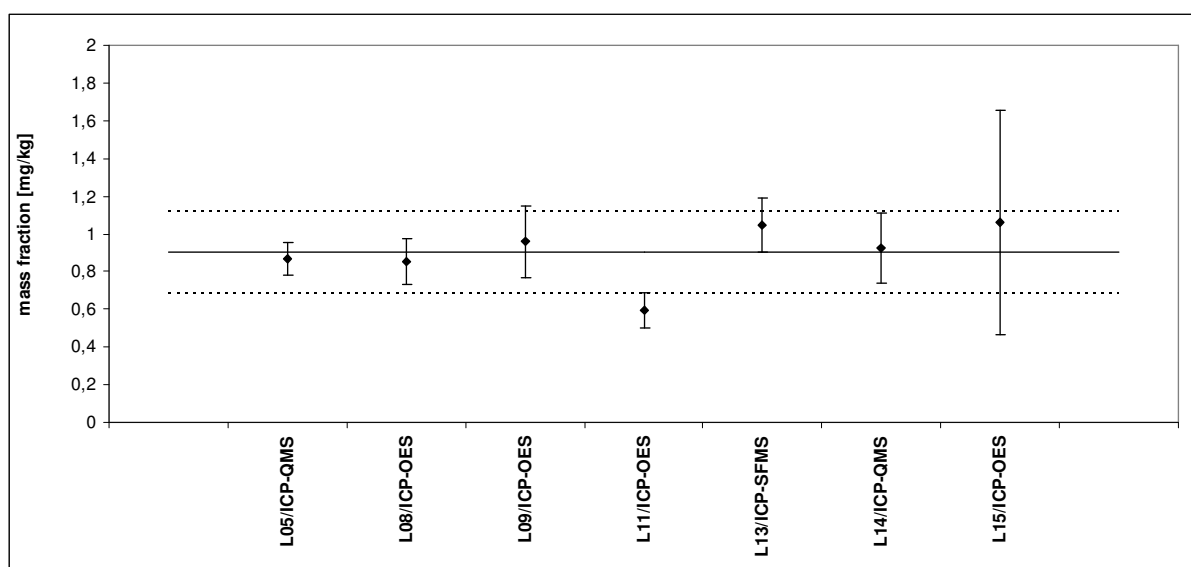
Lab code/Method	Excluded results [mg/kg]						Mean value [mg/kg]	s [mg/kg]	U_{Lab} [mg/kg]
L02/ICP-QMS	5.914	5.556	6.706	6.279	6.762	6.653	6.312	0.491	0.631
L03/ICP-SFMS	6.75	7.36	6.25	7.75	9.02	5.85	7.16	1.15	2.12
L04/ICP-QMS	4.32	4.42	4.42	4.16	4.51	4.78	4.44	0.21	0.19
L06/ICP-QMS	7.50	8.66	8.70	8.32	7.58	8.56	8.22	0.54	1.23
L07/ICP-QMS	9.49	8.79	8.13	9.26	8.77	8.14	8.76	0.56	2.54
L09/ICP-OES	7.158	8.012	8.382	8.503	10.008	8.434	8.416	0.926	0.581
L10/AAS-vapour system	13.0	11.0	10.5	12.5	11.0	10.5	11.4	1.1	3.7
L15/HAFS	7.527	7.373	8.940	7.242	7.115	6.535	7.455	0.803	1.935

Cadmium

Lab code/Method	Individual results ^a [mg/kg]						Mean value [mg/kg]	s [mg/kg]	U_{Lab} [mg/kg]
L05/ICP-QMS	0.895	0.839	0.875	0.850	0.870	0.859	0.865	0.020	0.086
L08/ICP-OES	0.936	0.936	0.868	0.827	0.790	0.764	0.854	0.065	0.119
L09/ICP-OES	0.969	0.977	0.998	0.995	0.918	0.889	0.958	0.032	0.192
L11/ICP-OES	0.636	0.598	0.615	0.556	0.628	0.526	0.593	0.043	0.091
L13/ICP-SFMS	0.997	0.988	1.055	1.025	1.149	1.060	1.046	0.065	0.144
L14/ICP-QMS	0.931	0.921	0.920	0.941	0.884	0.968	0.927	0.022	0.185
L15/ICP-OES	1.036	1.043	1.029	1.087	1.090	1.067	1.059	0.029	0.106

^a: values reported on mass of the sample after conditioning the sample using conditions as described in EN12341

Error bars in the graph represent expanded uncertainties (U_{Lab}) as reported by the participating laboratories. Solid line represents the certified value. Broken lines represent the expanded uncertainty of the certified value.



Excluded results were not used for the calculation of the certified value.

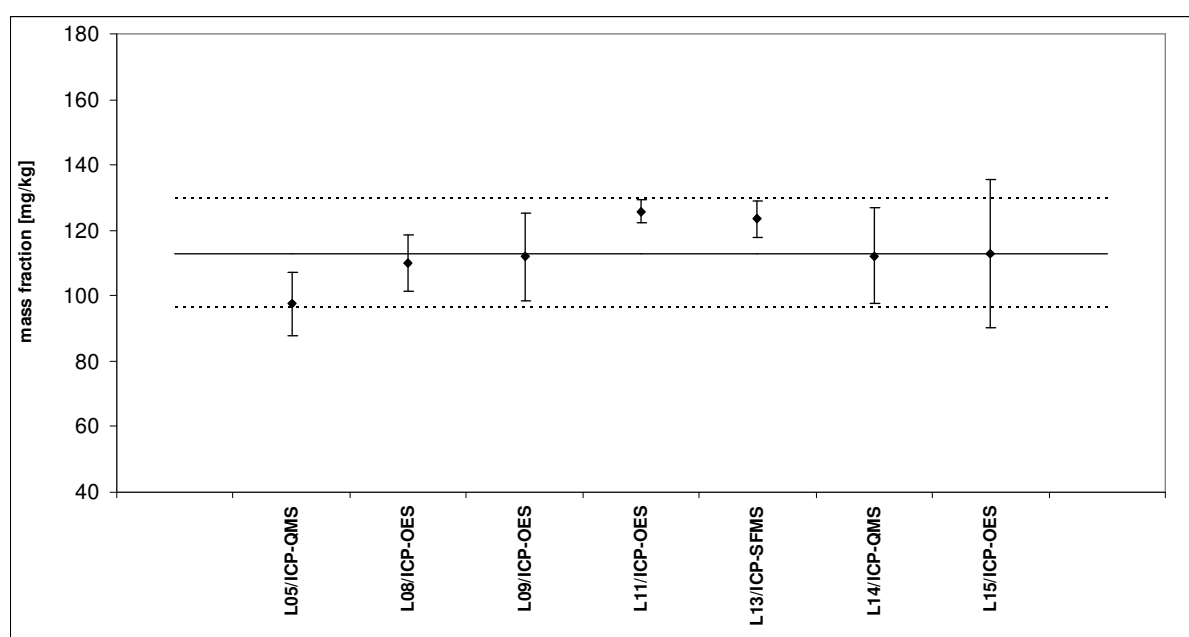
Lab code/Method	Excluded results [mg/kg]						Mean value [mg/kg]	s [mg/kg]	U_{Lab} [mg/kg]
L02/ICP-QMS	1.046	0.894	1.097	1.098	1.093	1.107	1.056	0.082	0.158
L03/ICP-SFMS	< 3	< 3	< 3	< 3	< 3	< 3	-	-	-
L04/ICP-QMS	0.763	0.7	0.796	0.766	0.792	0.766	0.76	0.03	0.035
L06/ICP-QMS	0.59	0.62	0.56	0.69	0.50	0.60	0.59	0.06	0.09
L07/ICP-QMS	2.12	1.99	2.17	1.80	2.14	2.02	2.04	0.14	-
L10/FAAS	1.0	0.5	1.0	0.5	1.0	0.5	0.8	0.27	0.150
L12/k0-NAA	< 3.1	< 2.8	< 3.5	< 3.2	< 3	< 2	-	-	-

Lead

Lab code/Method	Individual results ^a [mg/kg]						Mean value [mg/kg]	s [mg/kg]	U_{Lab} [mg/kg]
L05/ICP-QMS	96.4	96.1	99.2	96.2	99.0	98.2	97.5	1.4	9.8
L08/ICP-OES	112.8	110.3	105.7	109.6	112.8	108.6	110.0	2.7	8.8
L09/ICP-OES	110.9	111.5	109.4	113.6	110.4	115.5	111.9	2.3	13.4
L11/ICP-OES	128	123	125	125	127	126	126	2	4
L13/ICP-SFMS	118.2	130.1	120.9	123.3	121.5	126.9	123.5	4.3	5.5
L14/ICP-QMS	112.8	111.7	111.0	112.7	112.8	111.8	112.1	0.7	14.6
L15/ICP-OES	111.5	111.9	116.2	111.0	113.9	113.5	113.0	1.9	22.6

^a: values reported on mass of the sample after conditioning the sample using conditions as described in EN12341

Error bars in the graph represent expanded uncertainties (U_{Lab}) as reported by the participating laboratories. Solid line represents the certified value. Broken lines represent the expanded uncertainty of the certified value.



Excluded results were not used for the calculation of the certified value.

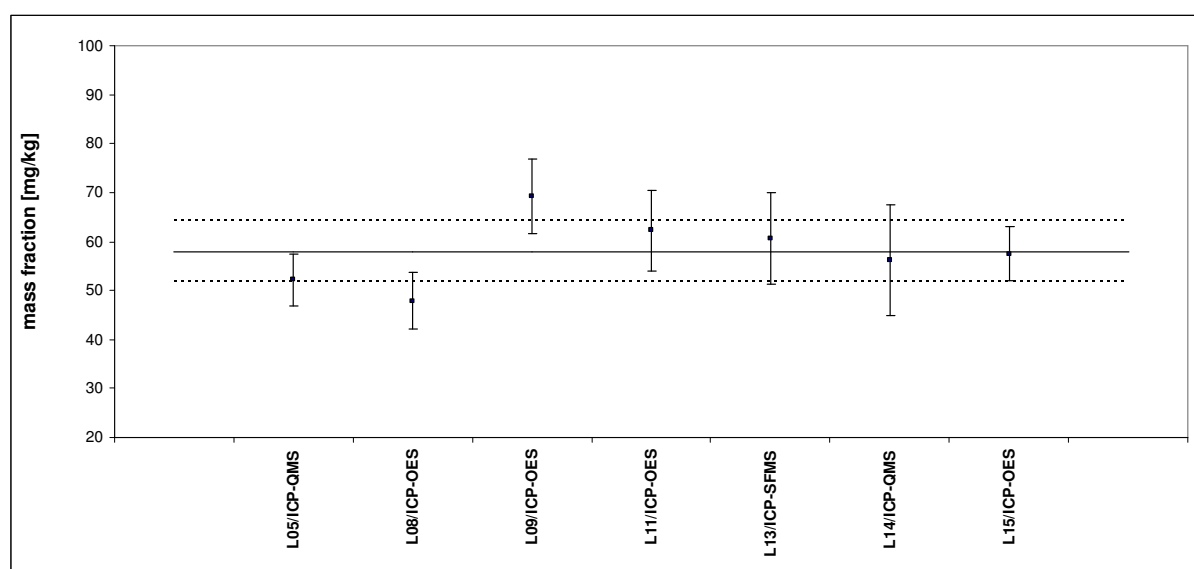
Lab code/Method	Excluded results [mg/kg]						Mean value [mg/kg]	s [mg/kg]	U_{Lab} [mg/kg]
L02/ICP-QMS	108.3	99.6	111.5	113.9	110.4	113.5	109.53	5.3	16.4
L03/ICP-QMS	123	117	125	136	129	123	126	6	22
L04/ICP-OES	80.4	82.9	79.7	79.7	82.1	80.6	80.9	1.3	1.4
L06/ICP-OES	78.8	95.6	98.1	103	91.0	107	95.6	9.9	9.6
L07/ICP-QMS	119.3	116.2	120.2	123.0	117.6	114.8	118.5	3.0	16.7
L10/FAAS	90.0	98.5	94.0	77.5	66.0	54.5	80.1	17.3	28.0

Nickel

Lab code/Method	Individual results ^a [mg/kg]						Mean value [mg/kg]	s [mg/kg]	U_{Lab} [mg/kg]
L05/ICP-QMS	57.0	51.2	51.5	51.0	51.3	50.9	52.2	2.4	5.2
L08/ICP-OES	50.7	51.4	45.2	50.4	44.8	44.9	47.9	3.2	5.7
L09/ICP-OES	68.929	73.456	65.859	70.63	68.805	67.944	69.271	2.573	7.620
L11/ICP-OES	69.7	58.2	58.8	63.0	62.7	61.2	62.3	4.1	8.3
L13/ICP-SFMS	60.4	59.2	61.3	62.6	60.7	58.9	60.5	1.4	9.3
L14/ICP-QMS	56.28	55.47	56.46	56.83	55.66	56.57	56.21	0.54	11.24
L15/ICP-OES	57.83	57.41	57.83	57.67	57.62	56.54	57.48	0.49	5.53

^a: values reported on mass of the sample after conditioning the sample using conditions as described in EN12341

Error bars in the graph represent expanded uncertainties (U_{Lab}) as reported by the participating laboratories. Solid line represents the certified value. Broken lines represent the expanded uncertainty of the certified value.



Excluded results were not used for the calculation of the certified value.

Lab code/Method	Excluded results [mg/kg]						Mean value [mg/kg]	s [mg/kg]	U_{Lab} [mg/kg]
L02/ICP-QMS	60.44	55.44	67.13	63.75	67.6	68.96	63.89	5.16	6.39
L03/ICP-SFMS	54.6	53.7	60.0	63.9	64.2	56.4	58.8	4.6	15.3
L04/ICP-OES	40.0	40.5	40.7	39.7	40.2	41.2	40.4	0.5	0.6
L06/ICP-OES	43.60	48.10	50.30	42.20	41.80	47.90	45.65	3.57	4.57
L07/ICP-QMS	56.48	55.79	59.38	58.86	56.91	58.09	57.59	1.41	5.27
L10/FAAS	47.0	83.5	78.5	89.0	104.5	85.0	81.3	19.0	14.6

Annex G: Additional material information, ERM-CZ120

Lab/method code	Element	Replicates [mg/kg]						Mean value [mg/kg]	s [mg/kg]
L01/k ₀ -NAA	Aluminium	34100	34400	34400	33800	34000	33900	34100	253
	Antimony	62.1	62.3	62.6	62.0	62.9	64.0	62.7	0.7
	Barium	534	536	541	560	536	549	543	10
	Bromine	9.7	9.7	9.7	9.6	9.8	10.2	9.8	0.2
	Caesium	2.93	2.94	2.91	2.86	2.97	3.01	2.94	0.05
	Calcium	63800	64000	62000	62000	64600	66900	63883	1829
	Cerium	58.9	56.2	55.0	54.0	57.2	58.3	56.6	1.9
	Chlorine	10000	9900	10400	10000	10000	9900	10033	186
	Chromium	199	196	194	189	198	203	197	5
	Cobalt	14.1	13.9	14.1	13.9	14.1	14.3	14.1	0.2
	Copper	480	440	500	420	460	470	462	29
	Dysprosium	3.29	3.57	2.70	3.50	3.10	3.60	3.29	0.35
	Europium	0.68	0.63	0.71	0.73	0.71	0.64	0.68	0.04
	Gallium	8.5	8.8	8.4	8.5	8.6	9.1	8.7	0.3
	Gold	0.029	0.025	0.020	0.028	0.014	0.015	0.022	0.007
	Hafnium	8.50	8.40	8.24	8.00	8.19	8.50	8.31	0.20
	Iron	37400	36800	37500	36700	37100	38200	37283	549
	Lanthanum	24.6	24.9	24.6	24.8	24.8	24.8	24.8	0.1
	Magnesium	13400	13000	13600	13000	13300	12900	13200	276
	Manganese	613	605	629	606	607	605	611	9
	Molybdenum	27.0	28.0	35.0	40.0	30.3	34.0	32.4	4.9
	Neodymium	-	-	-	-	-	-	-	-
	Potassium	10600	10800	10700	10700	10800	10900	10750	105
	Rubidium	50.4	49.0	48.8	47.6	51.0	51.8	49.8	1.6
	Samarium	4.14	3.49	3.94	4.06	4.05	4.29	4.00	0.27
	Scandium	7.24	7.17	7.21	7.09	7.22	7.39	7.22	0.10
	Sodium	13800	13900	13600	13600	13900	14000	13800	167
	Strontium	243	244	230	234	241	244	239	6
	Tantalum	1.02	0.96	0.97	0.95	0.97	0.98	0.98	0.02
	Terbium	0.552	0.553	0.528	0.530	0.538	0.520	0.537	0.013
	Thorium	6.88	6.79	6.61	6.62	6.8	6.95	6.78	0.14
	Titanium	4260	4500	4530	4340	4300	4300	4372	114
Tungsten	4.15	4.17	4.20	3.90	4.06	4.24	4.12	0.12	
Uranium	2.49	2.80	2.12	2.04	2.43	2.79	2.45	0.32	
Vanadium	72.0	71.9	74.0	72.2	73.5	70.8	72.4	1.16	
Ytterbium	1.32	1.24	1.77	1.76	1.25	1.32	1.44	0.25	
Zinc	1190	1180	1210	1180	1190	1220	1195	16	
Zirconium	331	340	320	310	325	338	327	11	

Annex G: Additional material information, ERM-CZ120

Lab/method code	Element	Replicates [mg/kg]						Mean value [mg/kg]	s [mg/kg]
L12/k ₀ -NAA	Aluminium	-	-	-	-	-	-	-	-
	Antimony	68.7	66.1	66.5	67.5	65.8	65.5	66.7	1.2
	Barium	591	580	579	587	574	579	582	6
	Bromine	10.4	10.0	10.4	11.4	10.9	10.9	10.7	0.5
	Caesium	3.23	3.09	3.19	3.18	3.14	3.15	3.16	0.05
	Calcium	62170	61450	63540	61400	60070	64580	62202	1625
	Cerium	57.4	55.9	57.2	57.1	56.5	57.2	56.9	0.6
	Chlorine	-	-	-	-	-	-	-	-
	Chromium	207	202	207	204	203	208	205	2
	Cobalt	14.6	14.3	14.8	14.6	14.6	14.6	14.6	0.2
	Copper	-	-	-	-	-	-	-	-
	Dysprosium	-	-	-	-	-	-	-	-
	Europium	0.89	1.01	0.98	0.96	0.99	1.02	0.97	0.05
	Gallium	-	-	-	-	-	-	-	-
	Gold	-	-	-	-	-	-	-	-
	Hafnium	8.45	8.38	8.49	8.49	8.46	8.55	8.47	0.06
	Iron	39180	38430	39460	38860	39020	39080	39005	345
	Lanthanum	25.5	24.6	25.2	25.3	25.3	25.2	25.2	0.3
	Magnesium	-	-	-	-	-	-	-	-
	Manganese	-	-	-	-	-	-	-	-
	Molybdenum	34.8	33.5	34.3	35.5	33.2	33.2	34.1	0.9
	Neodymium	22.6	20.9	20.7	22.8	24.5	21.8	22.2	1.4
	Potassium	11380	11220	11390	11280	10930	11280	11247	168
	Rubidium	56.1	55.7	54.0	55.0	53.5	55.2	54.9	1.0
	Samarium	4.21	4.13	4.14	4.18	4.14	4.14	4.16	0.03
	Scandium	7.63	7.51	7.66	7.57	7.59	7.61	7.59	0.05
	Sodium	14650	14380	14780	14600	14640	14680	14622	133
	Strontium	246	244	275	283	257	270	262	16
	Tantalum	1.09	1.05	1.07	1.10	1.05	1.04	1.07	0.02
	Terbium	0.59	0.57	0.59	0.60	0.60	0.58	0.59	0.01
	Thorium	7.34	7.10	7.10	7.18	7.14	7.21	7.18	0.09
	Titanium	-	-	-	-	-	-	-	-
	Tungsten	-	-	-	-	-	-	-	-
	Uranium	2.73	2.77	2.57	2.73	2.76	2.75	2.72	0.08
Vanadium	-	-	-	-	-	-	-	-	
Ytterbium	1.92	1.92	1.93	1.95	2.01	1.90	1.94	0.04	
Zinc	1289	1269	1301	1282	1282	1288	1285	11	
Zirconium	360	360	349	353	367	344	355	8	

Element	Replicates [mg/kg]	Mean value [mg/kg]	s [mg/kg]	Method of determination
Elemental carbon	43600 45500 47200	45433	1801	Coulometric titration
Silicon	229100 230700 227200	229000	1752	X-ray fluorescence spectroscopy
Total carbon	112000 111000 111000	111333	577	Coulometric titration
Total organic carbon	77100 76500 76300	76633	416	Coulometric titration

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Title: The Certification of the Mass Fractions of Arsenic, Cadmium, Nickel and Lead in Fine Dust (PM₁₀-like matrix), Certified Reference Material ERM[®]-CZ120

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Abstract

This report describes the preparation and certification of the new Reference Material (CRM) ERM-CZ120, which is a PM₁₀-like fine dust, certified for the elements arsenic, cadmium, nickel and lead.

Certification of the CRM included testing of the homogeneity and stability of the material as well as the characterisation using an intercomparison approach.

The main purpose of the material is to assess method performance, i.e. for checking accuracy of analytical results in the field of air quality control/measurement. As any reference material, it can also be used for control charts or validation studies.

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