Institute for Reference Materials and Measurements

ERM European Reference Materials

# CERTIFICATION REPORT

# The Certification of the Mass Fraction of the Total Content and the Aqua Regia Extractable Content of Hg in Loam Soil

# ERM®-CC141

E.de Vos, E. Engin, A. Santoro, M. Ricci, A. Held

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## Summary

The certified reference material ERM-CC141 Loam Soil was released in 2010 and is certified for total and aqua regia extractable (according to ISO 11466 [1]) As, Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn. The material required additional studies for the assignment of certified values for the mass fraction of total and aqua regia extractable (according to ISO 11466 [1]) Hg due to insufficient quality of the result obtained for these measurands during the original characterisation study. For this reason, new laboratories were contracted to obtain additional data sets for the characterisation study and a new set of samples was analysed to assess the long term stability of the material. This report presents the result of the additional certification of the mass fraction of total and aqua regia leachable Hg in ERM-CC141 Loam soil.

| Total content | Mass fraction based on dry mass | |
|---|---|---|
| | Certified value [2] [mg/kg] | Uncertainty [2] [mg/kg] |
| Hg | 0.083 | 0.017 |
| Aqua regia extractable content[1] | Mass fraction based on dry mass | |
| | Certified value [2] [mg/kg] | Uncertainty [2] [mg/kg] |
| Hg | 0.080 | 0.008 |

1) As obtained according to ISO 11466 [1] (two laboratories used a modified procedure using microwave digestion).
2) Unweighted mean value of the means of accepted sets of data, each set being obtained in a different laboratory and/or with a different method of determination. The certified values are traceable to the SI.
3) Expanded uncertainty with a coverage factor $k = 2$ according to the Guide for the Expression of Uncertainty in Measurement [2], corresponding to a level of confidence of about 95 %.

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## Glossary

| | |
|---|---|
| AMA | advanced mercury analyser |
| ANOVA | analysis of variance |
| A.R. | aqua regia extractable |
| BCR | Community Bureau of Reference |
| CRM | certified reference material |
| CV-AAS | cold vapour atomic absorption spectrometry |
| CV-AFS | cold vapour atomic fluorescence spectrometry |
| DMA | direct mercury analyser |
| ERM | European Reference Material |
| FIAAS | flow injection atomic absorption spectrometry |
| ICP-HR -MS | inductively coupled plasma - high resolution - mass spectrometry |
| ICP-Q-MS | inductively coupled plasma - quadrupole - mass spectrometry |
| ID-ICP-MS | isotope dilution - inductively coupled plasma – mass spectrometry |
| ICP-OES | inductively coupled plasma – optical emission spectrometry |
| IRMM | Institute for Reference Materials and Measurements |
| ISO | International Organization for Standardization |
| IEC | International Electrotechnical Commission |
| $k$ | coverage factor |
| LTS | long term stability |
| RSD | relative standard deviation |
| $RSD_{average}$ | relative standard deviation of the mean of laboratory means |
| $RSE_{aveage}$ | relative standard error of the mean of laboratory means |
| s | standard deviation of the laboratory mean |
| $s_{bb,rel}$ | relative between-unit standard deviation |
| SI | International System of Units |
| p | number of accepted data sets |
| QC | quality control |
| $t_{\alpha,df}$ | critical *t*-value for specified confidence interval |
| $t_{sl}$ | proposed shelf-life |
| $u_{bb,\ rel}$ | standard uncertainty related to a possible between bottles heterogeneity |
| $u^{*}_{bb}$ | standard uncertainty related to a maximum between-unit heterogeneity that could be hidden by method repeatability |
| $u_{char,\ rel}$ | standard uncertainty of the material characterisation |
| $u_{CRM}$ | standard uncertainty of the certified value |
| $U_{CRM}$ | expanded uncertainty of the certified value |
| $u_{lts,\ rel}$ | standard uncertainty of the long-term stability |
| $u_{rect}$ | standard uncertainty of the data modelled as a rectangular distribution |
| $\bar{x}$ | average of all time points |
| $x_i$ | time point for each replicate |
| $\bar{y}$ | average of all results of a homogeneity study |

# 1. Introduction

The work presented in this report refers exclusively to the certification of the total content and the aqua regia leachable content of Hg (according to ISO 11466) in ERM-CC141 Loam Soil. This material is a certified reference material (CRM) that was released in 2010 to replace BCR-141R Calcareous loam soil, which is out of stock. Mercury was included in the original certification project, but some difficulties were encountered, resulting in an insufficient number of data sets in the characterisation study and a large uncertainty contribution from the long term stability study. Additional measurements were performed on the material (long term stability study, characterisation exercise) in order to establish a certified value with a more acceptable uncertainty for Hg.

Two parts of the certification process needed to be addressed specifically. Firstly, the characterisation study provided only 4 acceptable data sets for the total Hg content and 5 satisfactory data sets for the aqua regia extractable Hg content (according ISO 11466). The number of data sets was considered to be insufficient to carry out a meaningful statistical analysis to obtain a certified value and therefore a new characterisation campaign was organised, inviting new laboratories to provide additional quality data sets. Secondly, the uncertainty contribution of the long term stability study was unacceptably high as a result of high method variation so a new set of samples was selected from the original isochronous study and sent for analysis to determine the uncertainty contribution related to long term storage of the material.

The remaining steps in the original certification process of ERM-CC141 (e.g. homogeneity study, short term stability study) produced adequate results for both total and aqua regia leachable Hg and were not repeated here. Results were presented when relevant, but the

majority of the work that is not related to the characterisation and long term stability study (e.g. sampling and processing) was described in detail in the main certification report [3] and the reader is referred to that.

## 2. Participants

### 2.1 Project management and data evaluation

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

### 2.2 Long Term Stability Study

Institut "Jozef Stefan" (JSI), Department of Environmental Sciences, Ljubljana, Slovenia (measurements under the scope of ISO/IEC 17025 accreditation; SA, LP-90).

### 2.3 Characterisation (in alphabetical order)

ALS Laboratory Group, ALS Czech Republic, Prague, Czech Republic (measurements under the scope of ISO/IEC 17025; CAI, 521).

ALS Laboratory Group, ALS Scandinavia AB, Luleå, Sweden - (measurements under the scope of ISO/IEC 17025; SWEDAC-1087).

Bundesanhalt für Materialforschung und -prüfung (BAM) - Department of Analytical Chemistry - Reference Materials, Berlin, Germany (measurements under the scope of ISO/IEC 17025, DAP-PL-2614.14)

Centre National de la Recherche Scientifique (CNRS), Service Central d'Analyse, Solaize, France.

DSM Research BV, Geleen, The Netherlands (measurements under the scope of ISO 9001, Lloyd's 65091)

Energy Research Centre of the Netherlands (ECN), Petten, The Netherlands (measurements under the scope of ISO/IEC 17025, RVA, L135

Helmholtz Zentrum München, Deutsches Forschungszentrum für Gesundheit und Umwelt (GmbH), München, Germany (measurements under the scope of ISO/IEC 17025; DACH, DAC-PL-0141-01-10).

Istituto Superiore per la Protezione e la Ricerca Ambientale, Environmental Metrology Service, Rome, Italy (measurements under the scope of ISO/IEC 17025, SIT nr. 211).

Institut "Jozef Stefan" (JSI), Department of Environmental Sciences, Ljubljana, Slovenia (measurements under the scope of ISO/IEC 17025 accreditation; SA, LP-90).

LGC Ltd, Teddington, United Kingdom (measurements under the scope of ISO/IEC 17025; UKAS, 0003).

The Macaulay Institute, Analytical Service, Aberdeen, United Kingdom (measurements under the scope of ISO/IEC 17025; UKAS, 1917).

Minton Treharne & Davies Ltd (MTD), Herbert J Evans Division, Carmarthenshire, United Kingdom (measurements under the scope of ISO/IEC 17025; UKAS, 0024).

Państwowy Instytut Geologiczny, (Polish Geological Institute), Warszawa, Poland (measurements under the scope of ISO/IEC17025, PCA, AB 283).

Umweltbundesamt GmbH, Prüfstelle für Umwelt-, GVO- & Treibstoff-Analytik, Wien, Austria (measurements under the scope of ISO/IEC 17025; BMWA-92.714/0518-I).

University of Barcelona, Department of Analytical Chemistry, Faculty of Chemistry, Barcelona, Spain.

University of Ferrara, Ferrara, Italy.

Universidad de Santiago, Facultad de Quimica, Departamento de Química Analítica, Santiago de Compostela, Spain.

Vlaamse Instelling voor Technologisch Onderzoek (VITO), Mol, Belgium (measurements under the scope of ISO/IEC 17025; BELAC, 045-TEST).

## 3. Material processing and process control

### 3.1 Sampling of the material

For the sample location and the sampling procedure, the reader is referred to the main certification report [3].

### 3.2 Processing

For the processing of the material the reader is referred to the main certification report [3].

## 4. Homogeneity

### 4.1 Between-unit homogeneity

The homogeneity of the total Hg content was assessed in a dedicated study. Sixteen bottles were selected throughout the produced batch in a random stratified manner [4]; three replicates per bottle were measured by CV-AFS (see Annex 1). For further details of the homogeneity study, the reader is referred to the main certification report [3].

The homogeneity of the aqua regia extractable content of Hg should have been assessed using the data from the short-term stability study (see main certification report [3]). However, the statistical analysis of the short-term stability data gave a result for the uncertainty contribution that was unacceptably high. Instead the homogeneity was assessed using the data from the long-term stability study (see paragraph 5). Fourteen bottles were used in the long-term stability study, which is two bottles less than the desired number of units for a homogeneity study (as a guideline, the number of units required for the homogeneity study is calculated as the cubic root of the total number of units produced of the material). Using the long-term stability data was nevertheless justified because the certified values of the total Hg content and the aqua regia extractable content are very similar, and because the high between-bottle

standard deviation of the short term stability data was caused by poor method repeatability. The statistical evaluation of the homogeneity study is presented in Table 1.

**Table 1: Summary of the statistical evaluation.**

| | **Sample means** | | | **Individual results** | | |
|---|---|---|---|---|---|---|
| | Distribution | Trend (filling sequence) | Outliers at 99% onfidence | Distribution | Trend (analytical sequence) | Outliers |
| **Total Hg** | Normal Unimodal | No | One | Normal Unimodal | No | One |
| **A.R. Hg**[1] | Normal Unimodal | No | None | Normal Unimodal | No | None |

[1] = aqua regia extractable Hg according to ISO 11466

The distribution of the data for both measurands followed a unimodal and approximately normal distribution. No trends were found in either the sample means or the analytical sequence. The data sets did however show an outlier in the data of the total Hg content, so calculation of the uncertainty contribution using ANOVA for this parameter was not appropriate. Instead a more cautious approach was taken by modelling the data as a rectangular distribution ($u_{rect}$), where the limit is determined by the largest outlying unit average. The uncertainty contribution from between-unit heterogeneity was then calculated as follows:

$$u_{rect} = \frac{\left|\text{largest outlier} - \bar{y}\right|}{\sqrt{3}} \qquad \text{Equation (1)}$$

$$u_{rect,rel} = \frac{u_{rect}}{\bar{\bar{y}}} \cdot 100\% \qquad \text{Equation (2)}$$

Where $\bar{y}$ = average of all results of the homogeneity study

Table 2 gives the calculated uncertainty contribution for the between bottle homogeneity $u_{bb,rel}$. For the total Hg content, the $u_{bb,rel}$ was taken as the larger value of the standard deviation between units ($s_{bb,rel}$) or as $u_{rec,\ rel}$; for the aqua regia extractable content the larger value of the $s_{bb,rel}$ or $u^*_{bb,rel}$ was taken.

**Table 2: Uncertainty contribution from between bottle heterogeneity**

| | **Mean concentration [mg/kg]** | $s_{bb,rel}$ **[%]** | $u^*_{bb}$ **[%]** | $u_{rect}$ **[%]** | $u_{bb,rel}$ **[%]** |
|---|---|---|---|---|---|
| **Total Hg** | 0.080 | 2.24 | 2.41 | 9.21 | 9.21 |
| **A.R. Hg**[1] | 0.076 | 2.17 | 1.54 | - | 2.17 |

[1] = aqua regia extractable Hg according to ISO 11466

The data for the dedicated homogeneity study can be found in Annex 1; the data of the long term stability study are presented in Annex 3.

### 4.2. Minimum sample intake

For the determination of minimum sample intake, the reader is referred to the main certification report [3]. The minimum sample intake for total Hg content was found to be 100 mg; for the aqua regia extractable Hg content, the ISO 11466 method prescribes a sample size of 3 g.

## 5. Stability

Stability studies are carried out to establish the conditions under which the material can be transported (short-term stability) and stored (long-term stability). The studies were carried out only for the aqua regia extractable fraction and the reason for taking this approach was that if changes should occur in the material as a result of transport or storage conditions, they would have a greater effect on the aqua regia extractable fraction of Hg than on the total Hg content. For more information regarding the set up of the short-term stability study of ERM-CC141, the reader is referred to the main certification report [3]. No significant trend was found in the tested conditions, so the data confirms that ERM-CC141 does not need special precautions for transport. The data for the short term stability study can be found in Annex 2.

### 5.1 Long term stability study.

The results of the original long term stability study (LTS) yielded an uncertainty contribution that exceeded that which was permitted in the project planning and the data was rejected (for details on the set up of this study, see the main certification report [3]). Samples were still available from the original isochronous study for ERM-CC141, so another set of samples was selected from this batch and sent to an external laboratory to obtain a new set of data for the long term stability. The samples were selected from the isochronous study at 18 $^{o}$C and covered the time points 0, 4, 8, 12, 16 and 24 months. Two units from normal stock (which is stored at 18 $^{o}$C) were added to the sample set to provide an additional data point for 36 months. The data presented and discussed here refers only to this new study.

The results were grouped and evaluated for each time point and temperature. Results were screened for outliers by applying the Grubbs test at confidence levels of 99 %. Data were

plotted against time and the regression lines were calculated to check for significant trends which would indicate degradation of the material. The observed slopes were tested for significance using a *t*-test, with $t_{\alpha,df}$ being the critical *t*-value (two-tailed) for a significance level $\alpha = 0.01$ (99 % confidence interval).

No significant slope was found under the tested conditions. The uncertainty of stability $u_{lts}$ of the material was calculated as uncertainty of the slope of the regression line multiplied by the chosen shelf life [5]:

$$u_{lts,\,rel} = \frac{s}{\sqrt{\sum \left(x_i - \bar{x}\right)^2}} . t_{sl} \qquad \text{Equation (3)}$$

Where *s* is the standard deviation of all 36 individual results of the stability studies, $x_i$ is the point for each replicate, $\bar{x}$ is the average of all time points and $t_{sl}$ is the pre-defined shelf-life. As the $u_{lts}$ for the other measurands certified in ERM-CC141 was calculated for a shelf-life of 36 months, the same was done for Hg. The result is presented in Table 3. A graphical representation of the long term stability can be found in Annex 3.

**Table 3. Results of the long-term stability study**

| | **18 °C** | | |
|---|---|---|---|
| | Outliers at 99% confidence level | Slope significance at 99% confidence level | $u_{lts}$ [%] |
| **A.R. Hg**[1] | No | No | 2.449 |

[1] aqua regia extractable Hg according to 11466

The $u_{lts}$ is included as one of the contributions to the overall uncertainty budget of the assigned certified values. After the certification campaign, the material will be subjected to IRMM's regular stability monitoring program to control its further stability.

# 6. Characterisation

## 6.1 Study set up

The characterisation of the material was done by means of an interlaboratory exercise. The laboratories contracted for the work were selected on the basis of demonstrated expertise in the field of trace element analysis (supported by documentation proving their measurement capabilities) and quality criteria (e.g. successful participation in proficiency testing schemes and/or previous characterisation exercises). Accreditation for the analyses required was an asset. All analyses had to be performed using validated methods. Most of the participating laboratories were accredited to ISO/IEC 17025 [6]. If the measurements are covered by the scope of accreditation, the accreditation is stated in the list of participants (see Section 2). Non-accredited laboratories were asked to provide separate evidence of compliance of the quality systems with the requirements prescribed in ISO/IEC 17025 [6].

The following precautionary measures were taken in the study set up:

1) To demonstrate absence of method bias, completely different and independent analytical methodologies were chosen for the determination of the same parameter, aiming at a minimum of 2 laboratories providing results per method.

2) Each laboratory had to provide six independent measurements, i.e. a new sample preparation had to be performed for each measurement. Moreover, to ensure within-laboratory reproducibility conditions, the measurements had to be spread over two days following an analytical sequence prescribed by IRMM.

3) A quality control sample, namely BCR-141R, a soil based reference material certified for total and aqua regia leachable content according to ISO 11466 [1] for a range of trace

elements including Hg, was sent along as a blinded sample and the results were used to support the evaluation of the characterisation results.

4) The samples were selected using a random stratified sampling scheme, covering the entire batch of candidate reference material.

Laboratories received two units of the candidate reference material ERM-CC141. Three independent measurements had to be performed on each unit. The laboratories were asked to provide one independent measurement for the quality control sample. The laboratories were provided with guidelines for the measurements, which included the approximate concentration range for both parameters to help them set up the correct range for the calibration.

Two of the laboratories used a modified procedure for the aqua regia extractable content compared to the one prescribed in ISO 11466 [1]. In those cases, samples were treated with the aqua regia acid mixture in combination with microwave heating. Work published by Nieuwenhuize *et al* [7] and Sastre *et al* [8], showed that microwave digestion with aqua regia offers a good alternative to traditional reflux extraction, providing comparable and accurate results. In the present study, the aqua regia leaching results obtained for the quality control sample (BCR-141R) using the modified procedure with microwave digestion were not found to be significant different from the certified values so the data sets were retained. The methods used for the determination of the total Hg content were based on microwave of pressure digestion in the presence of strong acids (HF, $HNO_3$, HCl or $HClO_4$), possibly with the addition of $H_3BO_3$.

### 6.2 Dry mass determination

The water content had to be determined on separate sub-samples. The water content measurements had to be carried out by drying a separate sample of at least 1 g in an oven at (105 ± 2) $^{o}$C until constant weight was achieved (usually for not less than 3 hours). The results for total and aqua regia extractable of Hg were reported in mass fractions based on dry mass.

### 6.3 Evaluation of results

A detailed overview of the analytical techniques used by the laboratories is given in Annex 4. The results collected from the participating laboratories are presented in Annex 5. All data was subjected to technical evaluation and data sets were rejected if laboratories had reported technical problems and/or if the results of the QC were inconsistent with the certified value as assessed following ERM Application Note 1 [9]. A summary of the data evaluation is presented in Table 4.

**Table 4. Summary of the technical evaluation**

| | | **Total Hg** | **Aqua regia extractable Hg** |
|---|---|---|---|
| **L0** | ICP-MS | QC failed | QC failed |
| **L1** | CV-AAS | QC failed | RSD out of specification |
| **L2** | ICP-MS | QC failed | QC failed |
| **L3** | CV-AAS | OK | OK |
| **L4** | CV-AAS | 2) | OK |
| **L5** | ICP-MS | 2) | OK |
| **L6** | ICP-SF-MS | OK | OK |
| **L7** | ICP-OES | 2) | 2) |
| **L8** | ID-ICP-MS | QC failed | 2) |
| **L9**[1)] | DMA | OK | 2) |
| **L10** | ICP-OES | OK | 2) |
| **L11** | ICP-SF-MS | 2) | OK |
| **L12** | ICP-MS | 2) | OK |
| **L13** | ICP-MS | QC failed | QC failed |
| **L14** | AMA | OK | OK |
| **L15** | ICP-MS | QC failed | Rejected |
| **L16** | CV-AAS | QC failed | Technical difficulties reported |
| **L17** | ICP-MS | OK | OK |
| **L18** | DMA | OK | 2) |
| **L19** | CV-AAS | OK | OK |
| **L20** | DMA | OK | 2) |
| **L21** | AMA | OK | OK |
| **L22** | CV-AFS | 2) | QC failed |
| **L23** | FIAAS | 2) | QC failed |

1) L9 did 9 measurements spread over two days (two sets of replicates on day one, one set of replicates on day two)
2) Laboratory was not contracted to do this analysis

The following data sets were discarded:

L0: the results for both parameters were discarded because the results reported for the QC sample did not match the certified value

L1: the result for the total Hg content was not accepted because the results reported for the QC sample did not match the certified value. The result for the aqua regia extractable fraction was not accepted because the relative standard deviation on the mean results was too high (RSD on the two units of candidate reference materials were 84 and 91 % respectively)

L2: the results for both parameters were discarded because the results reported for the QC sample did not match the certified value.

L8: the results for the total Hg content was not accepted because the results reported for the QC sample did not match the certified value.

L13: the results for both parameters were discarded because the results reported for the QC sample did not match the certified value.

L15 and 16: the results represented by these codes refer to one laboratory that measured both parameters with two different techniques. The results obtained for the total Hg content of the QC sample did not match that of the certified value by either technique. In the analysis of the aqua regia extractable content, the lab experienced technical problems for the analysis by ICP-MS. The cause of the problem was identified and the repeated analysis yielded the right result for the QC sample. However, because of the technical difficulties and the fact that the data set for total Hg content were unacceptable (which constitutes 50 % of all reported results) all data from this lab was rejected.

L22: the results for the aqua regia extractable Hg content was not accepted because the results reported for the QC sample did not match the certified value.

L23: the results for the aqua regia extractable Hg content was not accepted because the results reported for the QC sample did not match the certified value.

Following the technical assessment, ten data sets were accepted for both parameters. The accepted data sets were subjected to statistical analysis, including tests for outlying laboratory means using Dixon, Grubbs and Nalimov t-test (99% confidence interval), for normality of means distribution using kurtosis/skewness tests and for outlying variances using Cochran tests. A summary of the statistical analysis of the accepted data sets is presented in Table 5 (*s* stands for the standard deviation of the laboratory mean).

**Table 5. Statistical evaluation of technically accepted data sets**

| | **Number of individual data** | **Outlier means** | **Normality** | ***s* [mg/kg]** |
|---|---|---|---|---|
| **Total Hg** | 63 | None | Yes | 0.010 |
| **A.R. Hg**[1] | 60 | None | Yes | 0.007 |

[1] aqua regia extractable Hg according to 11466

Both data sets followed approximately normal distributions. Therefore the average value and the standard deviation can be used as the meaningful estimators for the expected value and its variation. The characterisation results are given in Table 6, expressed as the mean of means of the accepted data sets. The relative standard error of the mean is used as an estimation of the uncertainty contribution of the characterisation exercise ($u_{char,rel}$).

**Table 6. Result of the characterisation study**

| | **Mean of means [mg/kg]** | ***p*** | **$RSD_{average}$ [%]** | **$RSE_{average}$ [%] $u_{char,rel}$** |
|---|---|---|---|---|
| **Total Hg** | 0.083 | 10 | 11.5 | 3.64 |
| **A.R. Hg**[1] | 0.080 | 10 | 9.33 | 2.95 |

[1] aqua regia extractable Hg according to 11466
*p*: number of accepted data sets

## 7. Certified values and uncertainties

The certified values of ERM-CC141 Loam soil were calculated as the unweighted mean of the means of the accepted data sets as shown in Table 7. The certified uncertainty consists of uncertainties related to characterisation ($u_{char}$), between-bottle homogeneity ($u_{bb}$) and long-term storage ($u_{lts}$).

- $u_{char}$ was estimated as the standard error of the mean of laboratory means, i.e. $s/p$, where $s$ and p are taken from Table 5 and 6.

- $u_{bb}$ was taken as the larger value of the standard deviation between-units ($s_{bb}$) and the maximum heterogeneity hidden by method repeatability ($u^*_{bb}$), or as $u_{rect}$ (see paragraph 4.1).

- $u_{lts}$ was estimated from the results of a three year isochronous study at 18°C projected for a shelf life of 36 months.

These uncertainties were combined quadratically to estimate the expanded relative uncertainty of the certified value $U_{CRM,rel}$ according to the following formula:

$$U_{CRM,rel} = k\sqrt{u_{bb,rel}^2 + u_{lts,rel}^2 + u_{char,rel}^2} \qquad \text{Equation (4)}$$

The coverage factor $k = 2$ is chosen to provide a confidence level of approximately 95 %.

The absolute expanded uncertainty $U_{CRM}$ is calculated by rounding up the value obtained by multiplying the certified value with the relative expanded uncertainty $U_{CRM,rel}$. Table 7 presents the uncertainty budget with the individual uncertainty contributions, the expanded uncertainties and the certified values.

**Table 7. Certified values and uncertainty budget for total and aqua regia extractable Hg in ERM-CC141 Loam soil.**

| | $u_{bb,rel}$ [%] | $u_{lts,rel}$ [%] | $u_{char,rel}$ [%] | $U_{CRM,rel}$ ($k$=2) [%] | Certified Value [mg/kg] | $U_{CRM}$ ($k$=2) [mg/kg] |
|---|---|---|---|---|---|---|
| **Total Hg** | 9.21 | 2.45 | 3.64 | 20.4 | 0.083 | 0.017 |
| **A.R. Hg**[1] | 2.17 | 2.45 | 2.95 | 8.81 | 0.080 | 0.008 |

[1] aqua regia extractable Hg according to 11466

Annex 5 summarises the results of the characterisation exercise and gives a graphical representation of the assigned values together with the average values and uncertainties of the individual laboratories for both parameters.

## 8. Metrological traceability

Please refer to the main certification report [3].

## 9. Commutability

Please refer to the main certification report [3].

## 10. Instructions for use and intended use

Please refer to the main certification report [3].

## References

[1] ISO 11466 (1995) Soil quality - Extraction of trace elements soluble in aqua regia, Geneva, Switzerland

[2] ISO/IEC Guide 98-3:2008, Uncertanty of measurement - Part 3: Guide to the expression of uncertainty in measurement (GUM:1995), Geneva, Switzerland

[3] A. Birgersson-Liebich, T. Venelinov, A. Santoro, A. Held. Certification of the mass fraction of the total and aqua regia extractable content of As, Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn in loam soil - ERM-CC141. EUR Report 24486 - European Community, Luxembourg - 2010 - ISBN 978-92-79-16556-6.

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[5] A. Lamberty, H. Schimmel, J. Pauwels, The study of the stability of reference material by isochronous measurements, Fresenius J Anal Chem 360 (1998) 359 – 361.

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## Acknowledgements

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# Annexes

## Annex 1. Results of the homogeneity study

### 1.1 Total Hg content in ERM-CC141 [mg/kg]

| Unit number | Replicate 1 | Replicate 2 | Replicate 3 |
|---|---|---|---|
| **192** | 0.078 | 0.079 | 0.076 |
| **362** | 0.087 | 0.085 | 0.079 |
| **795** | 0.083 | 0.077 | 0.074 |
| **945** | 0.077 | 0.074 | 0.073 |
| **1108** | 0.08 | 0.079 | 0.076 |
| **1587** | 0.082 | 0.118 | 0.077 |
| **1760** | 0.08 | 0.075 | 0.081 |
| **1958** | 0.096 | 0.08 | 0.081 |
| **2043** | 0.08 | 0.079 | 0.08 |
| **2388** | 0.075 | 0.08 | 0.074 |
| **2765** | 0.081 | 0.078 | 0.079 |
| **3054** | 0.078 | 0.078 | 0.077 |
| **3381** | 0.078 | 0.075 | 0.079 |
| **3435** | 0.08 | 0.083 | 0.075 |
| **3783** | 0.076 | 0.079 | 0.08 |
| **4081** | 0.074 | 0.083 | 0.084 |

**1.2 Aqua regia extractable Hg content of ERM-CC141 (data from the long term stability study [mg/kg])**

| Unit number | Replicate 1 | Replicate 2 |
|---|---|---|
| **21** | 0.0739 | 0.0755 |
| **431** | 0.0771 | 0.0752 |
| **1403** | 0.0791 | 0.0771 |
| **1481** | 0.0758 | 0.0783 |
| **1971** | 0.0734 | 0.0731 |
| **2069** | 0.0758 | 0.0778 |
| **2073** | 0.0743 | 0.0727 |
| **2565** | 0.0743 | 0.0727 |
| **2992** | 0.0854 | 0.0797 |
| **3094** | 0.0744 | 0.0825 |
| **3134** | 0.0791 | 0.0756 |
| **3407** | 0.0768 | 0.0727 |
| **3497** | 0.0707 | 0.0778 |
| **4091** | 0.0755 | 0.0764 |
| **21** | 0.0739 | 0.0755 |
| **431** | 0.0771 | 0.0752 |

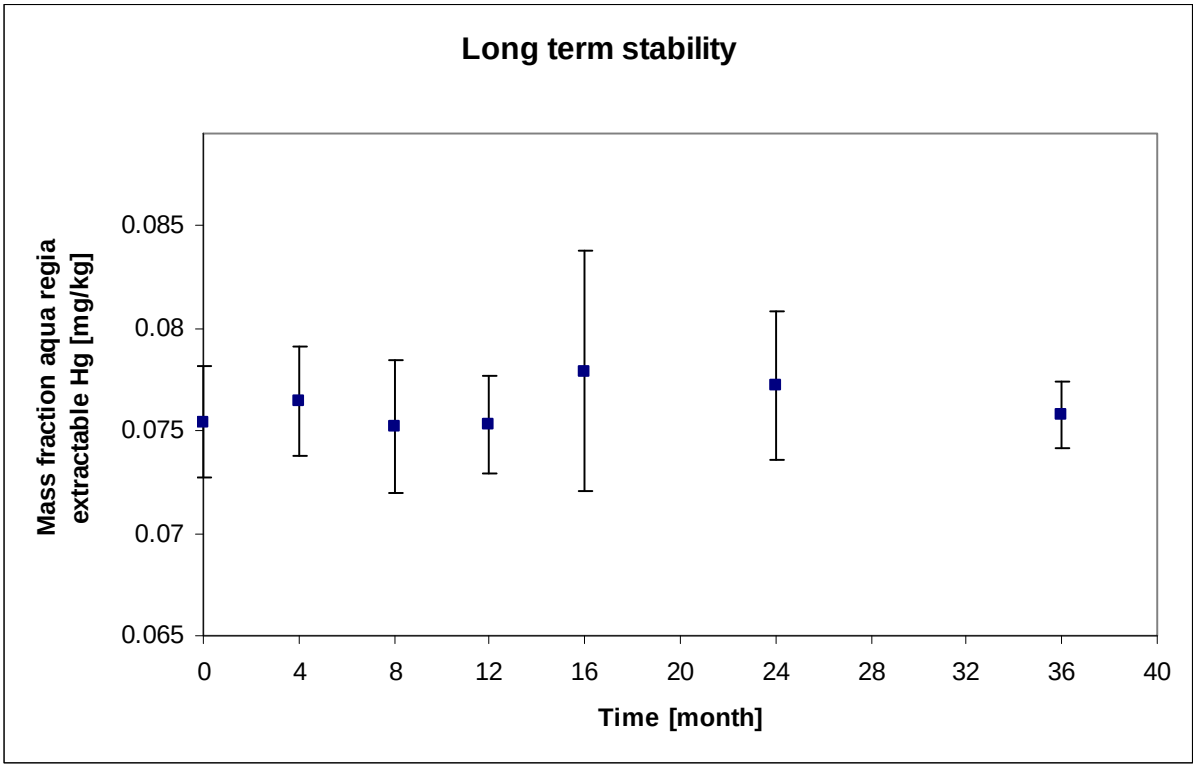
## Annex 2. Results of the short term stability study

| Unit | Replicate 1 | Replicate 2 | Replicate 3 |
|---|---|---|---|
| **74** | 0.08 | 0.09 | 0.12 |
| **343** | 0.09 | 0.1 | 0.1 |
| **511** | 0.07 | 0.09 | 0.1 |
| **799** | 0.09 | 0.09 | 0.09 |
| **924** | 0.11 | 0.11 | 0.1 |
| **1037** | 0.09 | 0.11 | 0.09 |
| **1195** | 0.23 | 0.15 | 0.09 |
| **1369** | 0.07 | 0.09 | 0.11 |
| **1442** | 0.07 | 0.1 | 0.09 |
| **1488** | 0.09 | 0.09 | 0.1 |
| **1629** | 0.1 | 0.09 | 0.13 |
| **1872** | 0.07 | 0.1 | 0.13 |
| **2541** | 0.07 | 0.11 | 0.09 |
| **2762** | 0.12 | 0.09 | 0.09 |
| **2849** | 0.1 | 0.1 | 0.09 |
| **3027** | 0.11 | 0.1 | 0.1 |
| **3253** | 0.07 | 0.13 | 0.1 |
| **3639** | 0.1 | 0.14 | 0.1 |
| **3854** | 0.07 | 0.1 | 0.09 |
| **3984** | 0.1 | 0.11 | 0.09 |
| **4067** | 0.07 | 0.08 | 0.1 |

**Annex 3. Results of the long term stability data**

**Aqua regia extractable Hg in ERM-CC141 according to ISO 11466.**

The data for the long-term stability study at 18 $^{o}$C is presented in Annex 1.2. The graphs report unit averages per time point and their 95 % confidence intervals based on the standard deviation of the measurements per time



## Annex 4. Summary of analytical techniques used in the characterisation of ERM-CC141

### 4.1 Total Hg content

| Lab code | Sample pre-treatment | Analytical method | Calibration |
|---|---|---|---|
| **L0** | Microwave digestion with $HNO_3$, HCL and HF | ICP-MS<br>Internal standard: Rh | Linear calibration<br>0.001 - 0.004 - 0.01 mg/L; metal salt in acid (VWR) |
| **L1** | Microwave digestion with $HNO_3$, HCL and HF | CV-AAS | External calibration<br>0 - 0.0025 - 0.005 - 0.0075 - 0.01 mg/L; $Hg(NO_3)_2$ (Panreac) |
| **L2** | Microwave digestion with $HNO_3$, HCL and HF | ICP-MS | External calibration<br>0 - 0.0002 - 0.0005 - 0.001 - 0.005 - 0.01 mg/L; $Hg(NO_3)_2$ (Panreac) |
| **L3** | Microwave digestion using $HNO_3$, HCl and HF of 0.3 g sample | CV-AAS | External calibration<br>0.00005 - 0.0001 - 0.0002 - 0.0003 - 0.0004 - 0.0005 - 0.0006 - 0.0008- 0.001 mg/L; ICP standard solution (Baker) |
| **L6** | Microwave digestion using $HNO_3$, HCl and HF | ICP-HR-MS<br>Internal standard: Lu<br>$CH_4$ gas mode<br>Mass resolution: 400 | External calibration<br>0-0.005; ICP standard solution (Ultra Scientific) |
| **L8** | Microwave digestion using $HNO_3$, HCl and HF of 0.2 g sample spiked with enriched isotopes | ID-ICP-MS with collision cell and cold vapour generator | NIST certified solution SRM 3133 |
| **L9** | | DMA according to EPA7473 method | 23 reference materials with mercury levels ranging from 0.03 to 8.6 mg/kg Hg |
| **L10** | Pressure assisted digestion using $HNO_3$ and $HCLO_4$ | CV-AFS | External calibration<br>0-1 ug/kg (NIST solution SRM 3133) |

### 4.1 Total Hg content - continued

| | | | |
|---|---|---|---|
| **L13** | Microwave digestion of 100 mg samples using $HNO_3$, HCl and HF, with addition of $H_3BO_3$ for a second digestion step | ICP-HR-MS<br>Internal standard: Rh and Ir<br>Mass resolution: 300 | External; calibration<br>0 - 0.2 - 0.5 - 1.0 - 2.0 - 5.0 - 10.0 µg/L; Hg standard solution (CPI) |
| **L14** | | AMA | External calibration<br>9 calibration points with concentrations ranging from 0 to 900 ng (Mercury ICP standard CertiPUR) |
| **L15** | Microwave digestion using $HNO_3$ and HF | ICP-MS<br>Internal standard: Lu | External calibration<br>0 - 0.5 - 1.0 - 1.5 - 2.0 - 2.5 Hg single element standard (Merck) |
| **L16** | Microwave digestion using $HNO_3$ and HF | CV-AAS | External calibration<br>0 - 2 - 4 - 6 - 8 - 10; Hg single element standard (Merck) |
| **L17** | Microwave digestion according to EN13656 | ICP-MS<br>Internal standard: Bi | External calibration according to ISO6143:2001<br>0.00010 - 0.00030 - 0.00050 - 0.00072 mg/L; Hg certified reference material: product n.28941 (Fluka) |
| **L18** | | DMA | External calibration according to ISO6143:2001<br>0.0000 - 0.0580 - 0.1147 - 0.1706 - 0.2231 mg/kg; Hg certified reference material: product n.28941 (Fluka) |
| **L19** | Microwave digestion | CV-AAS | External calibration<br>0.25 - 0.5 - 0.75 - 1.00 ng; Hg standard solution (JSI) |
| **L20** | | DMA | External calibration<br>0.01 - 0.02 - 0.05 - 0.10 - 0.20 - 0.50 - 1.00 - 5.00 mg/L; Hg standard (JSI) |
| **L21** | | AMA | External calibration<br>0.5 - 1.0 - 1.5 - 2 - 5 - 10 - 20 - 30 - 40 ng; Hg standard (Inorganic Venture) |

### 4.2 Aqua regia extractable Hg content according to the standard method ISO 11466

| Lab | Analytical method | Calibration | Comments |
|---|---|---|---|
| **L1** | CV-AAS | External calibration<br>0 - 0.0025 - 0.005 - 0.0075 - 0.01 mg/L; $Hg(NO_3)_2$ (Panreac) | |
| **L2** | ICP-MS | External calibration<br>0 - 0.0002 - 0.0005 - 0.001 - 0.005 - 0.01 mg/L; $Hg(NO_3)_2$ (Panreac) | |
| **L3** | CV-AAS | External calibration<br>0.00005 - 0.0001- 0.0002 - 0.0003 - 0.0004 - 0.0005 - 0.0006 -0.0008 - 0.001 mg/L; ICP standard solution (Baker) | |
| **L4** | CV-AAS | External;<br>0.00005 - 0.0001 - 0.0002 - 0.0003 - 0.0004 - 0.0005 - 0.0006 -0.0008 - 0.001 mg/L; ICP standard solution (Baker) | |
| **L5** | AMA | Linear;<br>0.01 mg/L (CRM Calibration solutions ASTASOL) | |
| **L6** | ICP-HR-MS<br>Internal standard: Lu<br>$CH_4$ gas mode<br>Mass resolution: 400 | External;<br>0 - 0.005, ICP standard solution (Ultra Scientific) | ISO 11466 modified with microwave digestion |
| **L11** | CV-AAS | Linear fit curve<br>6 calibration standards with concentrations ranging from 0 to 0.002 g/L; Hg standard solution (SPEX) | |
| **L12** | ICP-MS | Linear calibration<br>0 - 0.002 - 0.004 - 0.01 mg/L; Hg standard solution (BDH) | |
| **L13** | ICP-HR-MS<br>Internal standard: Rh and Ir<br>Mass resolution: 300 | External calibration<br>0 - 0.2 - 0.5 - 1.0 - 2.0 - 5.0 - 10.0 µg/L; Hg standard solution (CPI) | |
| **L14** | CV-AFS | External calibration<br>0 - 25 - 50 - 75 - 100 ng/L (Mercury ICP standard CertiPUR) | |

## 4.2 Aqua regia extractable Hg content according to the standard method ISO 11466 - continued

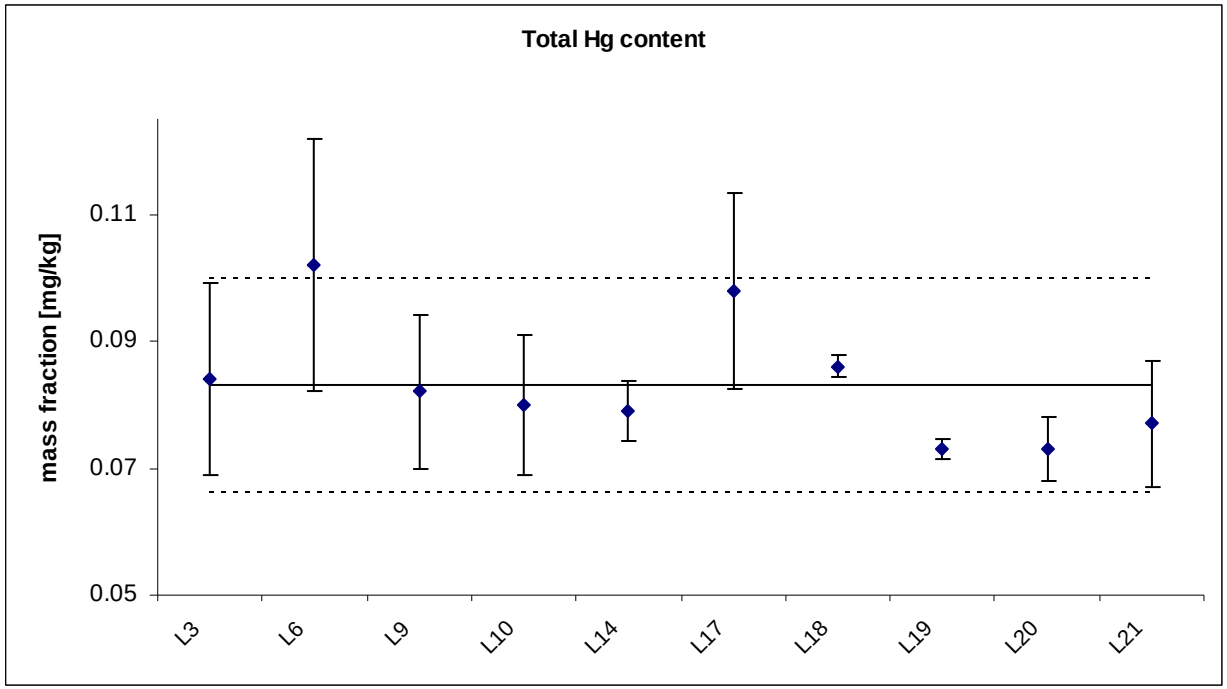
| | | | |
|---|---|---|---|
| **L15** | ICP-MS<br>Lu as internal standard | External calibration<br>0 - 0.5 - 1.0 - 1.5 - 2.0 - 2.5 Hg single element standard (Merck) | |
| **L16** | CV-AAS | External calibration<br>0 - 2 - 4 - 6 - 8 - 10; Hg single element standard (Merck) | |
| **L17** | ICP-MS<br>Bi as internal standard | External in according to ISO6143:2001;<br>0.00005 - 0.00020 - 0.00036 mg/L Hg certified reference material: product n.28941 (Fluka) | ISO 11466 modified with microwave digestion |
| **L19** | CV-AAS | External calibration<br>0.25 - 0.5 - 0.75 - 1.00 ng; Hg standard solution (JSI) | |
| **L21** | CV-AAS | External calibration<br>0.01 - 0.02 - 0.04 - 0.06 - 0.08 - 0.10 mg/L; Hg standard solution (Inorganic Venture) | |
| **L22** | CV-AFS | External calibration (linear with calculated intercept);<br>0.0000 - 0.0025 - 0.0050 - 0.0100- 0.0150 - 0.0200 mg/L; Hg standard for AAS (Fluka TraceCert) | |
| **L23** | CV-AFS | External calibration<br>0, 0.0002 - 0.0004 - 0.0008 - 0.0016 mg/L; Hg standard solution (Fluka TraceCert) | |

## Annex 5. Results of the characterisation study

The tables in this annex also contain the data sets that were discarded for technical reasons. These data sets are highlighted in italics and are given for information purposes only. They are not included in the graphs.

### 5.1 Results for total Hg [mg/kg]

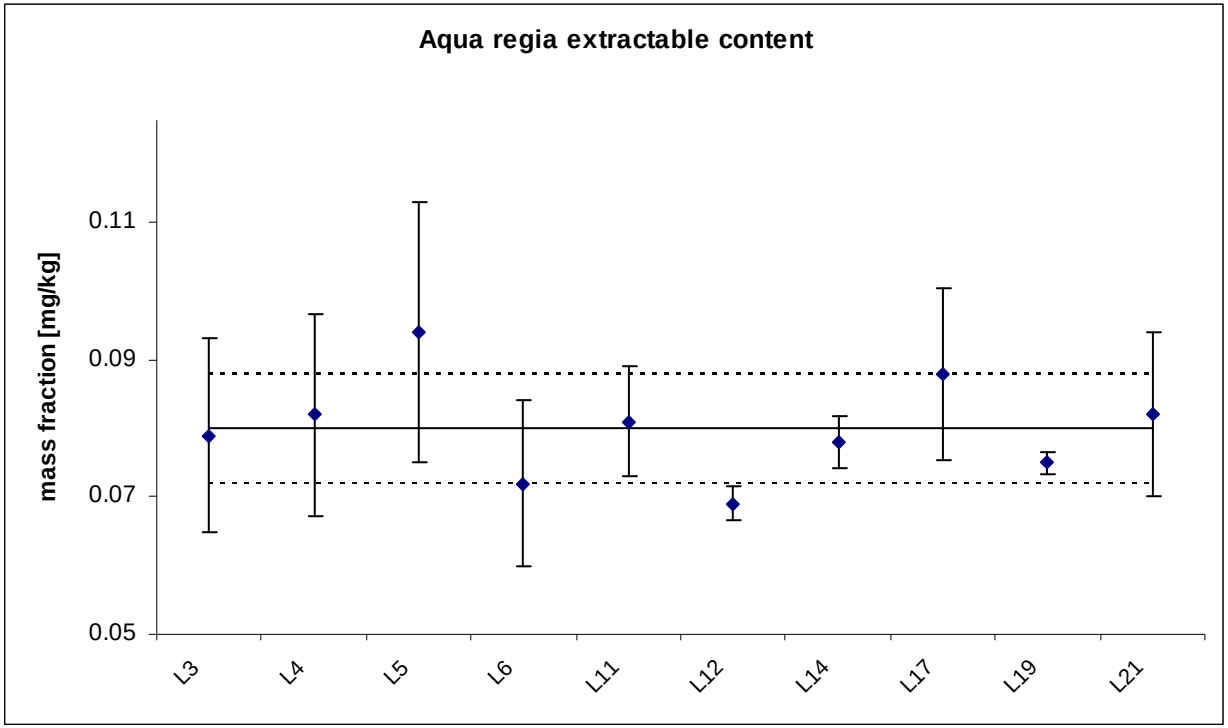
| Lab code | Sample 1 | Sample 2 | Sample 3 | Sample 4 | Sample 5 | Sample 6 | Sample 6 | Sample 6 | Sample 6 | Mean | $U_{char}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| ***L0*** | *0.800* | *0.400* | *0.500* | *0.600* | *0.300* | *0.500* | | | | *0.517* | *0.712* |
| ***L1*** | | *1.870* | *0.290* | *1.130* | *0.270* | *0.040* | | | | *0.920* | *0.755* |
| ***L2*** | *0.090* | *0.200* | *0.060* | *0.160* | | *0.220* | | | | *0.146* | *0.069* |
| **L3** | 0.085 | 0.084 | 0.083 | 0.083 | 0.087 | 0.081 | | | | 0.084 | 0.002 |
| **L6** | 0.112 | 0.097 | 0.106 | 0.091 | 0.102 | 0.101 | | | | 0.102 | 0.007 |
| ***L8*** | *0.090* | *0.078* | *0.098* | *0.075* | *0.082* | *0.094* | | | | *0.086* | *0.009* |
| **L9** | 0.081 | 0.089 | 0.083 | 0.079 | 0.083 | 0.081 | 0.086 | 0.079 | 0.080 | 0.082 | 0.003 |
| **L10** | 0.080 | 0.080 | 0.074 | 0.078 | 0.076 | 0.090 | | | | 0.08 | 0.006 |
| ***L13*** | *0.274* | *0.194* | *0.273* | *0.207* | *0.258* | *0.277* | | | | *0.247* | *0.037* |
| **L14** | 0.077 | 0.086 | 0.075 | 0.078 | 0.077 | 0.083 | | | | 0.079 | 0.004 |
| ***L15*** | *0.064* | *0.068* | *0.064* | *0.081* | *0.064* | *0.083* | | | | *0.071* | *0.009* |
| ***L16*** | *0.076* | *0.078* | *0.060* | *0.055* | *0.080* | *0.084* | | | | *0.072* | *0.012* |
| **L17** | 0.090 | 0.102 | 0.108 | 0.094 | 0.092 | 0.102 | | | | 0.098 | 0.007 |
| **L18** | 0.090 | 0.084 | 0.086 | 0.083 | 0.085 | 0.089 | | | | 0.086 | 0.003 |
| **L19** | 0.074 | 0.076 | 0.073 | 0.070 | 0.072 | 0.073 | | | | 0.073 | 0.002 |
| **L20** | 0.076 | 0.070 | 0.072 | 0.072 | 0.075 | 0.077 | | | | 0.073 | 0.003 |
| **L21** | 0.078 | 0.075 | 0.078 | 0.080 | 0.072 | 0.080 | | | | 0.077 | 0.003 |




Error bars represent expanded uncertainties as reported by participating laboratories. The solid line represents the certified values (the mean of laboratory means), while the broken lines represent the expanded uncertainty of the certified value.

## 5.2 Aqua regia extractable Hg content according to ISO 11466 [mg/kg]

| Lab code | Sample 1 | Sample 2 | Sample 3 | Sample 4 | Sample 5 | Sample 6 | Mean | $U_{char}$ |
|---|---|---|---|---|---|---|---|---|
| ***L0*** | *0.150* | *0.110* | *0.100* | *0.100* | *0.100* | *0.100* | *0.110* | *0.020* |
| ***L1*** | *0.080* | *0.410* | *0.230* | *0.470* | *0.130* | *0.060* | *0.230* | *0.174* |
| ***L2*** | *0.510* | *0.310* | *0.035* | *0.480* | *0.190* | *0.050* | *0.263* | *0.206* |
| **L3** | 0.082 | 0.074 | 0.077 | 0.080 | 0.084 | 0.075 | 0.079 | 0.004 |
| **L4** | 0.090 | 0.072 | 0.076 | 0.088 | 0.089 | 0.076 | 0.082 | 0.008 |
| **L5** | 0.091 | 0.095 | 0.097 | 0.094 | 0.093 | 0.095 | 0.094 | 0.002 |
| **L6** | 0.069 | 0.068 | 0.078 | 0.073 | 0.072 | 0.069 | 0.072 | 0.004 |
| **L11** | 0.087 | 0.083 | 0.080 | 0.081 | 0.078 | 0.075 | 0.081 | 0.004 |
| **L12** | 0.069 | 0.073 | 0.069 | 0.071 | 0.066 | 0.065 | 0.069 | 0.003 |
| ***L13*** | *0.080* | *0.081* | *0.079* | *0.077* | *0.081* | *0.075* | *0.079* | *0.002* |
| **L14** | 0.083 | 0.074 | 0.081 | 0.076 | 0.077 | 0.075 | 0.078 | 0.003 |
| ***L15*** | *0.084* | *0.072* | *0.066* | *0.072* | *0.073* | *0.070* | *0.073* | *0.002* |
| ***L16*** | *0.081* | *0.070* | *0.065* | *0.072* | *0.073* | | *0.072* | *0.003* |
| **L17** | 0.087 | 0.088 | 0.089 | 0.092 | 0.086 | 0.085 | 0.088 | 0.003 |
| **L19** | 0.075 | 0.075 | 0.075 | 0.073 | 0.075 | 0.076 | 0.075 | 0.001 |
| **L21** | 0.085 | 0.081 | 0.083 | 0.083 | 0.082 | 0.077 | 0.082 | 0.003 |
| ***L22*** | *0.095* | *0.095* | *0.089* | *0.118* | *0.095* | *0.089* | *0.097* | *0.004* |
| ***L23*** | *0.075* | *0.072* | *0.073* | *0.075* | *0.076* | *0.070* | *0.074* | *0.001* |




Error bars represent expanded uncertainties as reported by participating laboratories. The solid line represents the certified values (the mean of laboratory means), while the broken lines represent the expanded uncertainty of the certified value.

European Commission

**EUR 25141 EN – Joint Research Centre – Institute for Reference Materials and Measurements**
The Certification of the Mass Fraction of the Total Content and the Aqua Regia Extractable Content of Hg in LoamSoil - ERM®-CC141
E.de Vos, E. Engin, A. Santoro, M. Ricci, A. Held
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Abstract

The certified reference material ERM-CC141 Loam Soil was released in 2010 and is certified for total and aqua regia extractable (according to ISO 11466 [1]) As, Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn. The material required additional studies for the assignment of certified values for the mass fraction of total and aqua regia extractable (according to ISO 11466 [1]) Hg due to insufficient quality of the result obtained for these measurands during the original characterisation study. For this reason, new laboratories were contracted to obtain additional data sets for the characterisation study and a new set of samples was analysed to assess the long term stability of the material. This report presents the result of the additional certification of the mass fraction of total and aqua regia leachable Hg in ERM-CC141 Loam soil.

| Total content | Mass fraction based on dry mass | |
|---|---|---|
| | Certified value [2] [mg/kg] | Uncertainty [2] [mg/kg] |
| Hg | 0.083 | 0.017 |
| Aqua regia extractable content[1] | Mass fraction based on dry mass | |
| | Certified value [2] [mg/kg] | Uncertainty [2] [mg/kg] |
| Hg | 0.080 | 0.008 |

1) As obtained according to ISO 11466 [1] (two laboratories used a modified procedure using microwave digestion).

2) Unweighted mean value of the means of accepted sets of data, each set being obtained in a different laboratory and/or with a different method of determination. The certified values are traceable to the SI.

3) Expanded uncertainty with a coverage factor $k = 2$ according to the Guide for the Expression of Uncertainty in Measurement [2], corresponding to a level of confidence of about 95 %.

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