



EUROPEAN COMMISSION
DIRECTORATE-GENERAL
Joint Research Centre



23 June 2006
Revised Dec 2008

CCQM-K44

Trace Elements in Sewage Sludge FINAL REPORT

Y. Aregbe and P.D.P. Taylor

With contributions from:

J. Vogl from BAM
J. A. Salas and E. Zapata from CENAM
L. Valiente from INTI
C. Quétel, E. Vassileva and P. Robouch from IRMM
P. Vermaercke from SCK-CEN
G. Labarraque from LNE

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European Commission
Directorate-General Joint Research Centre
Institute for Reference Materials and Measurements

Contact information
Yetunde Aregbe
European Commission
Directorate-General Joint Research Centre
Institute for Reference Materials and Measurements
Retieseweg 111
B-2440 Geel • Belgium

Email: jrc-irmm-imep@ec.europa.eu

Tel.: +32 (0)14 571 673
Fax: +32 (0)14 571 865

<http://www.irmm.jrc.be>
<http://www.jrc.cec.eu.int>

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Abstract

CCQM-K44 was an activity of the Inorganic Analysis Working Group (IAWG) of CCQM and was coordinated by the Joint Research Centre-Institute for Reference Materials and Measurements (IRMM, Geel, Belgium) of the European Commission (EC). In CCQM-K44 the amount contents of Cd, Cr, Cu, Pb, Hg, Ni and Zn in sewage sludge were the measurands under investigation. Results were reported by 6 NMIs. During the CCQM-IAWG Spring meeting in Paris, April 2006, the approaches to calculate the KCRV as proposed by the coordinating laboratory were discussed and agreed on. The final report was submitted in June 2006. After the final report had been submitted to the CCQM in June 2006 the coordinating laboratory was informed that MIRS/IJS was not a designated institute and therefore could not represent the Slovenian NMI in CCQM-K44. This was contrary to what MIRS confirmed to the coordinating laboratory at the beginning of CCQM-K44. After several discussions between MIRS and the CCQM the coordinating laboratory was asked to amend the final report accordingly. In this revised version of the CCQM-K44 final report the results of MIRS/IJS were taken out of CCQM-K44 and included in the pilot study CCQM-P70, which was organised in parallel to CCQM-K44.

Due to the limited number of participants compared to previous key comparisons the mixture model median (MM-median) of all reported results could not be applied as KCRV for all the measurands. During the CCQM-IAWG Spring meeting in Paris, April 2006, the approaches to calculate the KCRV as proposed by the coordinating laboratory were discussed and first agreed on. As a result the final report and degrees of equivalence were finalised and submitted to the CCQM. Subsequent discussions between the IAWG and the CCQM were held, resulting in a different approach as proposed by the coordinating laboratory. Particularly Maurice Cox from NPL recommended the weighted

mean and its standard uncertainty ($k=1$) as KCVR independently of the number of participants. The coordinating laboratory agreed to this proposal and amended the final report using the weighted mean KCRV in CCQM-K44 for all measurands.

The reported results of the NMIs fall within a range of $\pm 4\%$ deviation from the KCRVs for Cr and Hg. For Pb and Cu the NMIs reported results within $\pm 9\%$. For Zn the spread of all laboratories but one is $\pm 2\%$. For Cd 2 of the 3 participating NMIs reported results within $\pm 0.2\%$ from the KCRV. The coordinating laboratory agreed with BAM, CENAM and LNE that due to the observed spread of the results Ni will be reported as inconclusive and no KCRV or degrees of equivalence for Ni will be included in this report.

The methods applied were isotope dilution mass spectrometry (IDMS) using quadrupole inductively coupled plasma-mass spectrometry (ICP-MS) or thermal ionisation mass spectrometry (TIMS), external calibration using atomic absorption spectrometry (AAS).

K_{σ} -neutron activation analysis (k_{σ} -NAA) and X-ray Fluorescence (XRF) were also used as analytical techniques.

This final report presents the participants' results in CCQM-K44 for all analytes under investigation. In Annex 1, the results with the KCRV, are presented. In Annex 2, the questionnaire data are presented.

The pilot study CCQM-P70 was carried out in parallel to this key comparison for the same measurands in the same sewage sludge material. Participation was meant for IAWG members, who did not immediately want to report results in a key comparison, and invited expert laboratories.

Introduction

At the April meeting 2004 in Paris it was decided to organise a key comparison CCQM-K44 and a pilot study CCQM-P70 using a sewage sludge material. The purpose of CCQM-K44&P70 was to demonstrate the measurement capability of determining the amount content of metals, which are regulated in international and national legislations, in a sewage sludge material originating from treatment of municipal sewage. The concentrations of the metals present in this sewage sludge material ranged over 3 orders of magnitude. Laboratories who demonstrate their capability of measuring the Cd, Cr, Cu, Hg, Ni, Pb and Zn amount content in the CCQM-K44 and CCQM-P70 sewage sludge sample, are likely to have the capability, knowledge and skills to measure the amount content of other elements at similar levels in other sludge, soil or sediment matrices which require similar sample preparation. Since sewage sludge is a 'dirty' matrix this material was from an analytical sample pretreatment point of view a challenging task, further broadening the scope and degree of difficulty of measurements in a key comparison addressed by the CCQM-IAWG.

The same sewage sludge material used in CCQM K44&P70 was measured by 204 laboratories in the frame of IMEP 21. The IMEP-21 participants' report is accessible via the IMEP web-site [1, 2].

Rationale of this comparison

Sewage sludge is the residue remaining from the treatment of municipal sewage. It is an organic-rich waste produced primarily by physical processes. Sewage contains aqueous domestic waste as well as surface drainage and, in many cases, a component of treated and untreated industrial effluent. Sewage sludge tends to concentrate a wide range of substances by absorbing or binding them to the organic matrix of the sludge. If not managed properly, untreated discharged sewage effluents can pose a high risk to

environmental resources and human health. The purification process enables reclaimed water to be discharged to freshwater courses or used in other applications under conditions that pose a greatly reduced risk to the receiving environment. Increased levels of waste water purification lead, inevitably, to greater quantities of sludge for which environmentally sound management strategies are required.

The European Union promotes the use of sewage sludge as fertilizer in agriculture. The Council Directive 86/278/EEC of 12 June 1986 sets rules for the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture. In this directive limit concentration ranges of metals in sewage sludge are laid down as follows [3].

mg·kg⁻¹ (dry mass)

Cd	20-40
Cu	1000-1750
Hg	16-25
Ni	300-400
Pb	750-1200
Zn	2500-4000

In national legislation the concentration ranges for metals can be set below these limits. The directive 86/278/EEC is discussed to be revised and lower levels for metals and most probably also upper levels for PCBs and PAHs concentrations will be included.

Participation in CCQM-K44

CCQM-K44 PARTICIPANT	COUNTRY
CCQM-K44 IAWG members	
BAM Bundesanstalt für Materialforschung und –prüfung	Germany
CENAM Centro Nacional de Metrología	Mexico
INTI Instituto Nacional de Tecnología Industrial	Argentina
IRMM Institute for Reference Materials and Measurements	European Commission
LNE Laboratoire National d'Essais	France

The sewage sludge sample

The sludge material originates from different sewage plants in Italy and France. The sample is a dried and milled sewage sludge blend bottled in amber glass bottles each one containing ~ 40 g of material. The range of metals amount content in this sewage sludge material was close to the limit concentration ranges as stated in the Council Directive 86/278/EEC [3]. Therefore, it was perfectly appropriate for the purpose of a CCQM key comparison and pilot study.

Homogeneity characterisation

Within, between bottle homogeneity and stability tests were carried out applying several analytical methods. For Cd, Hg and Pb solid sample Zeemann Atomic Absorption Spectrometry (SS-ZAAS) was carried out on 10 sub-samples of 10 bottles, furthermore additional tests were done on 3 to 5 sub-samples from 3 to 5 bottles applying IDMS for Cd, Hg, Pb and Zn. For Cu and Cr the homogeneity was assessed by analysing 3 sub-samples from 10 bottles applying k_{σ} -NAA. For Ni 3 sub-samples from 5 bottles applying IDMS and Atomic emission spectrometry (AES) were measured. Results from all these measurements were combined applying the analysis of variance ANOVA [4, 5]. The between bottle homogeneity of all measurands was ranging from 0.3% - 1%. As a result this material was found to be appropriate for the needs of this comparison. Further details on the methodology and results of homogeneity and short term stability characterisation can be found in the IMEP-21 certification report, which is publicly available via the IMEP web-site [1, 6].

Participant Coordination

According to the rules for participation in key comparisons only IAWG members who meet the requirements given in paragraph 6 of the MRA could participate in CCQM-K44 [7].

The call for participation was circulated to the NMIs in February/March 2005. The information package containing the sewage sludge samples was sent to all registered participants in May 2005. The participants were asked to register for participation and to report their results and questionnaire answers online via the IRMM IT system for Interlaboratory Comparisons, called MILC. The first deadline for result reporting was 20th September 2005. For one laboratory it was extended to 25th October 2005 due to delayed sample mailing. The normalised results were presented at the autumn IAWG meeting in October in Berlin. In January 2006, a summary report, including proposals for the KCRVs, was circulated amongst all participants for confirmation of the reported results and applied analytical methods. The draft report was circulated amongst participants in March 2006 and presented at the CCQM-IAWG meeting in Paris in April 2006.

CCQM-K44 information documents

- Letter to the participants pointing out the deadlines
- Scope of the CCQM-K44 key comparison
- General instructions
- Instructions for online result and questionnaire reporting in MILC
- Instructions for uncertainty evaluation
- Instructions for the dry-mass correction and digestion of the sewage sludge

Protocol for dry-mass correction

The determination of the moisture content of the samples is to some extent “operationally defined” [8, 9]. In view of the comparability of the results, the protocol in CCQM-K44 for correction of the moisture was as follows:

“The sewage sludge will absorb ambient moisture at typical laboratory temperature and humidity conditions. Therefore the sample bottle should only be opened immediately before weighing aliquots for the IDMS blend preparation. For correction of the measured values to dry mass, water content measurements should be made on a separate portion of the same material with a mass of 0.5 ± 0.1 g. The material should be dried before weighing for 24 hours in a ventilated oven at 105 ± 2 °C. The weighing has to be carried out after the sample has reached thermal equilibrium at room temperature in a desiccator, recommended time about 20 min. The loss of mass corresponds to the “dry-mass correction factor” that should be applied”. The water content was also determined by Karl-Fischer titration. No significant difference was observed. The reported results in CCQM-K44 for the measured water content in the sewage sludge are listed in Table 1

Uncertainty evaluation

The participants were asked to report a complete uncertainty budget with their results. The uncertainty statement should be evaluated and presented according to the principles outlined in, e.g. “ISO/GUM” [10] or the EURACHEM/CITAC Guide [11].

The organising laboratory asked all the participants in CCQM-K44 the following:

- state your measurement equation
- identify all significant sources of uncertainty
- state your input quantities
- quantify uncertainty components and convert them to standard uncertainties
- calculate the combined standard uncertainty u_c
- present an expanded uncertainty U with the coverage factor $k=2$

- include factors related to sample treatment in your measurement equations
- describe the applied evaluation process and type of assumed distribution for your uncertainty estimation

The complete uncertainty statement should be forwarded to the organising laboratory as attachment to the result reporting sheets.

All participants in CCQM-K44 provided a full report and a complete uncertainty budget with the measurement results.

Table 1 Reported values for water content determination and dry-mass correction

CCQM-K44 Correction for dry-mass		
PARTICIPANT	WATER CONTENT IN %	CORRECTION FACTOR
BAM	4.362 ± 0.042	0.9564 ± 0.0004
CENAM	$3.84 \pm <0.05$	1.0384 ± 0.014
EC-JRC-IRMM	5.64 ± 0.2	0.9436 ± 0.002
INTI	3.79 ± 0.1	1.039 ± 0.002
IRMM_SCK	5.64 ± 0.4	0.9436 ± 0.0036
LNE	4.7 ± 0.14	0.952 ± 0.0011

Analytical methods and techniques

Different methods and instrumental techniques besides IDMS were applied in CCQM-K44.

The methods applied were:

- isotope dilution mass spectrometry (IDMS) using quadrupole inductively coupled plasma-mass spectrometry (ICP-MS) or thermal ionisation mass spectrometry (TIMS)
- external calibration using atomic absorption spectrometry (AAS)
- k_0 -neutron activation analysis (k_0 -NAA)

- X-ray fluorescence (XRF)

The analytical methods and instrumental techniques are listed in Table 2.

Table 2 Analytical methods and instrumental techniques in CCQM-K44

CCQM-K44 analyte: Cd, Cr, Cu, Hg, Ni, Pb, Zn		
PARTICIPANT	ANALYTICAL METHOD	INSTRUMENTAL TECHNIQUE
BAM	IDMS	TIMS
CENAM	XRF, external calibration	WD-XRF
INTI	AAS, external calibration	Cd, Cr, Ni, Pb, Zn: FAAS Hg: CV-AAS
IRMM	Cd, Hg, Pb: direct IDMS Zn: double IDMS Cr, Cu: NAA	Cd, Hg, Pb, Zn: ICP-QMS Cr, Cu: k_0 -NAA
LNE	Cr, Cu, Ni, Pb, Zn: double IDMS	Cr, Cu, Ni, Pb, Zn: ICP-QMS

CCQM-K44 participant's result

The CCQM-K44 participants' results, as reported to the organising institute, are listed in Table 3.

Table 3 CCQM-K44 participants reported results

REPORTED RESULTS AND EXPANDED UNCERTAINTY ($k=2$) in 10^{-3} mol·kg $^{-1}$				
Participant	Cd	Cr	Cu	Hg
BAM	0.17087 ± 0.00075	3.882 ± 0.050	13.462 ± 0.051	-
CENAM	-	-	14.65 ± 1.10	-
INTI	0.15 ± 0.013	3.97 ± 0.48	-	0.0464 ± 0.0044
IRMM	0.1711 ± 0.0021	4.03 ± 0.19	13.1 ± 0.63	0.045 ± 0.0018
LNE	-	3.74 ± 0.097	13.65 ± 0.43	-

REPORTED RESULTS AND EXPANDED UNCERTAINTY ($k=2$) in 10^{-3} mol·kg $^{-1}$			
Participant	Ni	Pb	Zn
BAM	1.1697 ± 0.0082	2.842 ± 0.023	47.85 ± 0.10
BAM_corr.*	-	2.947 ± 0.023*	-
CENAM	2.67 ± 0.55	2.91 ± 0.22	55.60 ± 4.60
INTI	-	2.705 ± 0.091	48.1 ± 1.2
IRMM	-	2.991 ± 0.034	48.84 ± 0.22
LNE	1.079 ± 0.033	3.08 ± 0.083	46.64 ± 0.96

* BAM discovered after the results were presented at the CCQM-IAWG meeting in Berlin in Oct. 2005, that the final result for Pb was calculated with an incorrect Pb²⁰⁶ spike concentration, resulting from a typographic error. Since results cannot be amended after they have been presented to all participants, both results are listed in Table 3. Only the BAM result reported before the CCQM-IAWG autumn 2005 meeting was used for the calculation of the degrees of equivalence among institutes.

The CCQM-K44 KCRV

At the CCQM meeting in Paris in April 2004, David L. Duewer from NIST presented a robust approach for the determination of CCQM Key Comparison Values and Uncertainties to the IAWG members [12]. He introduced the mixture model probability density function (MM-PDF) for each measurement population as a means of data analysis for key comparisons and pilot studies. MM-PDF based summary statistics enable estimation of the expected performance of the majority of participants of a key comparison or pilot study [13]. The “true value” of a measurand in a given material can be estimated in a robust way even when some of the results are not in accordance with the majority. Originally the MM-median was proposed as KCRV for all the analytes in CCQM-K44 where the number of participants ≥ 4 . In this case, $n \geq 4$ the KCRV was calculated as $\mu \pm \sigma \cdot t_{\alpha} / \sqrt{n}$ which is the 95% confidence interval on μ for n reported results. For Hg and Ni with $n = 3$ the arithmetic mean was used as an estimate of the KCRV and calculated as $\mu \pm 2\sigma / \sqrt{n}$. IRMM suggested this as an acceptable approach to estimate the CCQM-K44 KCRV in case of $n < 4$.

This proposed approach to calculate the KCRVs for the measurands under investigation in CCQM-K44 was discussed and agreed on during the IAWG meeting in April 2006, at the BIPM in Paris. After submission of the final

report subsequent discussions between the IAWG and the CCQM were held, resulting in a different approach as proposed by the coordinating laboratory. Particularly Maurice Cox from NPL recommended the weighted mean and its uncertainty as KCRV independently of the number of participants. The coordinating laboratory agreed to this proposal and amended the final report using the weighted mean KCRV and its standard uncertainty ($k=1$) in CCQM-K44 for all measurands as listed in Table 4. BAM discovered after the results were presented at the CCQM-IAWG meeting in Berlin in Oct. 2005, that the final result for Pb was incorrect due to a typographic error. Taking into account that the originally reported BAM result was therefore not correct, the corrected BAM result for Pb was used to calculate the CCQM-K44 KCRV. After discussion with CENAM, the reported result for Ni was assumed to be biased. The coordinating laboratory agreed with BAM, CENAM and LNE that due to the observed spread of the results Ni will be reported as inconclusive and no KCRV will be included in this report. In the table below the KCRVs are listed for all the analytes in CCQM-K44.

Table 4 proposed KCRVs in CCQM-K44

$\mu \pm \sigma (k=1)$ in $10^{-3} \text{ mol}\cdot\text{kg}^{-1}$				
	Cd	Cr	Cu	Hg
KCRV_weighted mean	0.1708 ± 0.0014	3.862 ± 0.080	13.465 ± 0.076	0.04520 ± 0.00069

$\mu \pm \sigma (k=1)$ in $10^{-3} \text{ mol}\cdot\text{kg}^{-1}$			
	Ni	Pb	Zn
KCRV_weighted mean	inconclusive	$2.964 \pm 0.092^{**}$	48.01 ± 0.47

**without BAM reported but with BAM corrected result

The CCQM-K44 graphs

The CCQM-K44 results are presented graphically in Annex 1 of this report. All CCQM K44 results are plotted in ascending order, including the proposed KCRV. To enable the comparison of the spread of data, the scale of all graphs is $\pm 20\%$ deviation with respect to the KCRV.

The equivalence tables and equivalence charts are also plotted in Annex 1.

Table 5 summarises all the CCQM-K44 graphs of Annex 1

Table 5 CCQM-K44 graphs

General Graphs - Annex 1	Cd, Cr, Cu, Hg, Pb, Ni and Zn
All participants with KCRV	✓ (except Ni)
Equivalence charts	✓ (except Ni)

Discussion

Unfortunately the number of NMIs reporting results in CCQM-K44 was not as high as expected. Initially more NMIs expressed interest in participation, but did finally not register because of equipment or time schedule problems. Furthermore there might have been a difference in the level of experience between NMIs that have for years participated to similar key comparisons and others who have more recently joined the MRA. Nevertheless, as can be seen from Table 3 and the graphs in Annex 1, the agreement of measurement results between NMIs is good. The reported results of the NMIs fall within a range of $\pm 4\%$ deviation from the proposed KCRVs for Cr and Hg. For Pb the NMIs reported results within $\pm 9\%$ deviation from the proposed KCRVs. The reported results fall within a range of $\pm 2\%$ for Cu, including the CENAM result the spread increases to $\pm 9\%$. For Cd the reported results are within $\pm 0.2\%$, including the result from INTI the range increases to $\pm 12\%$. The reported results of the NMIs fall within a range of $\pm 2\%$ for Zn, including the result from CENAM within $\pm 16\%$.

BAM discovered after the results were presented at the CCQM-IAWG meeting in Berlin in Oct. 2005, that the final result for Pb

was calculated with an incorrect ^{206}Pb spike concentration, resulting from a typographic error. BAM sent the correct value for the spike concentration to IRMM with a corrected result for Pb. Since BAM could prove that the error was not an analytical, but a copy-paste error and taking into account that the originally reported BAM result was therefore not correct, the corrected BAM result for Pb was used to calculate the CCQM-K44 KCRV.

CENAM commented that they had encountered problems with their equipment during the measurements resulting in a biased Ni result. CENAM reported that the variation of the result is the consequence of the problems that they had with their equipment that did not work in stable conditions. About the bias, CENAM would like to continue to making new experiments in order to correct it. CENAM hopes to have another opportunity in the near future to participate with this kind of measurements in another study. The coordinating laboratory agreed with BAM, CENAM and LNE that due to the observed spread of the results Ni will be reported as inconclusive and no KCRV or degrees of equivalence for Ni will be included in this report.

CCQM-K44 Trace Elements in Sewage Sludge

It needs to be emphasised again that results cannot be amended after they have been presented to all participants, thus the BAM result originally reported before the CCQM-IAWG autumn 2005 was used in the calculation of the degrees of equivalence among institutes.

Conclusion

The material under investigation in this key comparison is an organic-rich waste produced primarily by physical processes. For destructive analysis participants had to consider carefully their approach in view of suitable digestion methods and acid mixtures. Furthermore the concentration ranges of the metals present in this sewage sludge material varied over a range of 3 orders of magnitude, from $50 \text{ mmol}\cdot\text{kg}^{-1}$ to $50 \text{ }\mu\text{mol}\cdot\text{kg}^{-1}$. All in all a challenging task as well from the analytical sample pre-treatment as from the measurement point of view.

The analytes under investigation in CCQM-K44 have been measured with 3 or 4 different analytical techniques. This confirms again the conclusion already drawn in previous key comparisons and pilot studies. Reliable measurements of highest metrological quality can be performed with various instrumental techniques (ICP-MS, AAS, NAA) and analytical methods (IDMS, external calibration, and non destructive analysis). They are not method dependent.

At the same time this comparison confirms that the main purpose of any Interlaboratory Comparison, thus also of CCQM comparisons, is to assess capabilities and to discover problems and correct analytical procedures accordingly. In this sense NIMs with a result significantly deviating from the KCRV immediately benefited from participating in CCQM K44. The organising laboratory appreciates that those laboratories are sharing this experience with all the other participants.

CCQM-K44 is also a good example of a key comparison in parallel to a pilot study involving not only the NIMs, but also expert laboratories of their countries as it is one of the NIMs' major tasks to disseminate metrological principles and good measurement practice to the laboratories in their countries. With the agreement of all participants, the final report of the pilot study CCQM-P70 will also be published in the metrologia technical supplement.

NIMs could prove with their participation in CCQM-K44 their measurement capabilities on measurements close to legal limits over a variety of metals and a wide range of concentrations. Furthermore they have demonstrated their capability on appropriate sample treatment for similar matrices such as sludge, soil and sediment. This key comparison therefore serves perfectly to support CMCs of those NIMs in Appendix C. For Ni participation in CCQM-K44 could not support CMC claims since due to the small number of participants and the observed spread of the results this part of the study was inconclusive.

Acknowledgements

Special thanks to F. Ulberth and A. Held from the RM unit for their support in providing the suitable sewage sludge sample and in the design of the homogeneity study. The authors acknowledge furthermore the input of all the scientists who contributed to the reprocessing and characterisation of the sewage sludge sample : - K. H. Grobecker, M. Bickel, A. Michiels, A. Bernreuther, S. Yazgan, P. Conneely, T. Prohaska, B. Sejerøe-Olsen, O. Bercau. Furthermore the assistance of all IMEP team members, particularly our MILC experts, S. Bynens and E. Garlick, is warmly acknowledged and the support of M. Sargent as chairman of the CCQM IAWG.

List of abbreviations

AAS	Atomic Absorption Spectrometry
AES	Atomic Emission Spectrometry
BIPM	Bureau International des Poids et Mesures (Paris, France)
CCQM	Comité Consultatif pour la Quantité de Matière
CITAC	Co-operation for International Traceability in Analytical Chemistry
CRMs	Certified Reference Materials
EC	European Commission
EU	European Union
EURACHEM	A focus for Analytical Chemistry in Europe
GUM	Guide for expression for Uncertainty in Measurement
IAWG	Working Group on Inorganic Analysis
ICP-MS	Inductively Coupled Plasma-Mass Spectrometry
IDMS	Isotope Dilution Mass Spectrometry
IRMM	Institute for Reference Materials and Measurements (EC, Geel, Belgium)
ISO	International Organisation for Standardisation
JRC	Joint Research Centre
K_0-NAA	Neutron Activation Analysis with k_0 standardization
MM-median	Mixture Model Median
MM-PDF	Mixture Model Probability Density Function
NAA	Neutron Activation Analysis
NMIs	National Metrology Institutes
SS-ZAAS	Solid Sample Zeemann Atomic Absorption Spectrometry
TIMS	Thermal Ionisation Mass Spectrometry
XRF	X-ray Fluorescence

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Annex 1 – Graphical presentation

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CCQM-K44: Trace Elements in Sewage Sludge

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Equivalence charts _____

CCQM-K44: Trace Elements in Sewage Sludge

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Figure 1

CCQM-K44: Cd in sewage sludge
 Weighted mean: $0.1708 \pm 0.0014 \cdot 10^{-3} \text{ mol}\cdot\text{kg}^{-1}$ [$\mu \pm \sigma$ ($k=1$)]

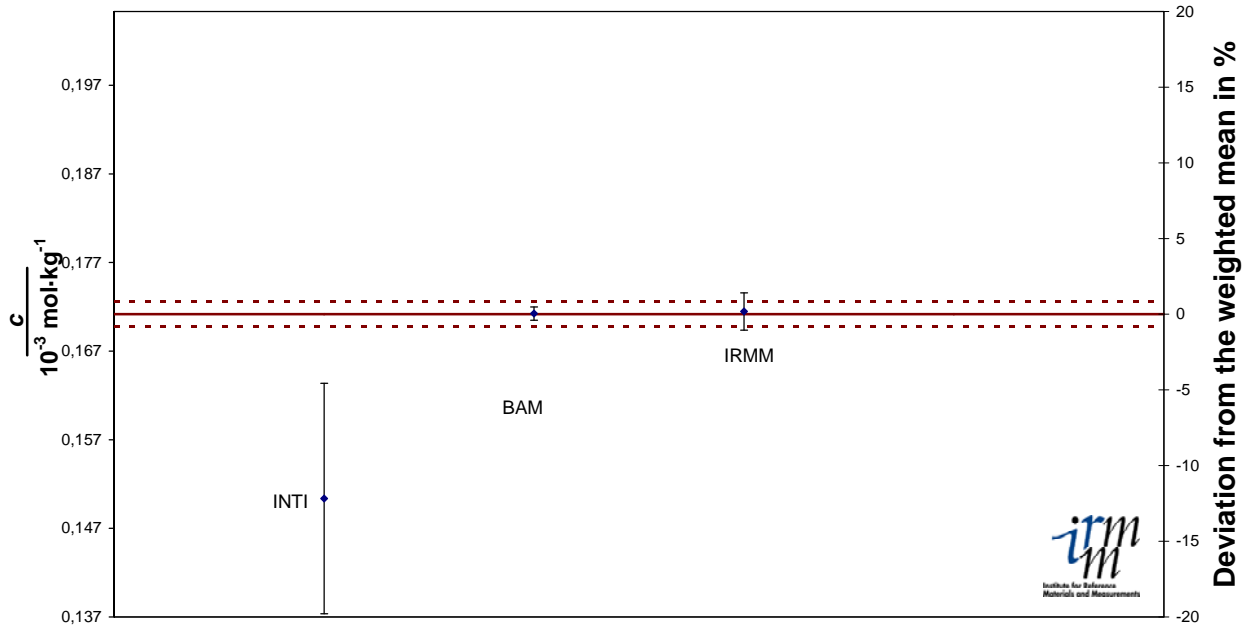


Figure 2

CCQM-K44: Cr in sewage sludge
 Weighted mean: $3.862 \pm 0.080 \cdot 10^{-3} \text{ mol}\cdot\text{kg}^{-1}$ [$\mu \pm \sigma$ ($k=1$)]

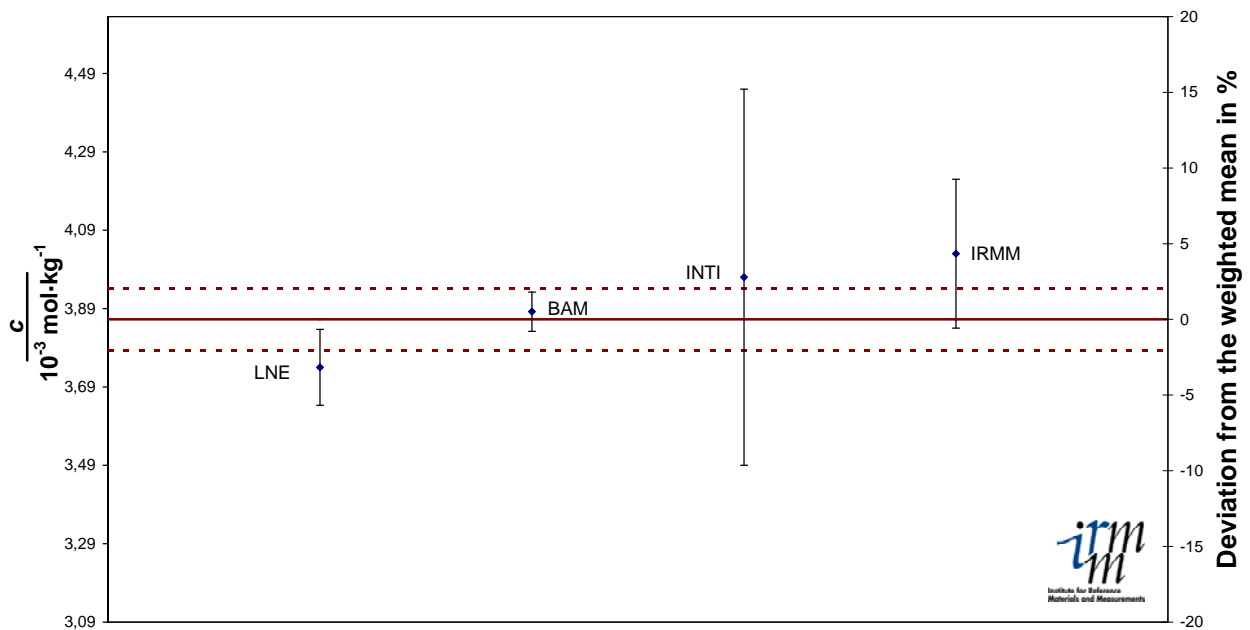


Figure 3

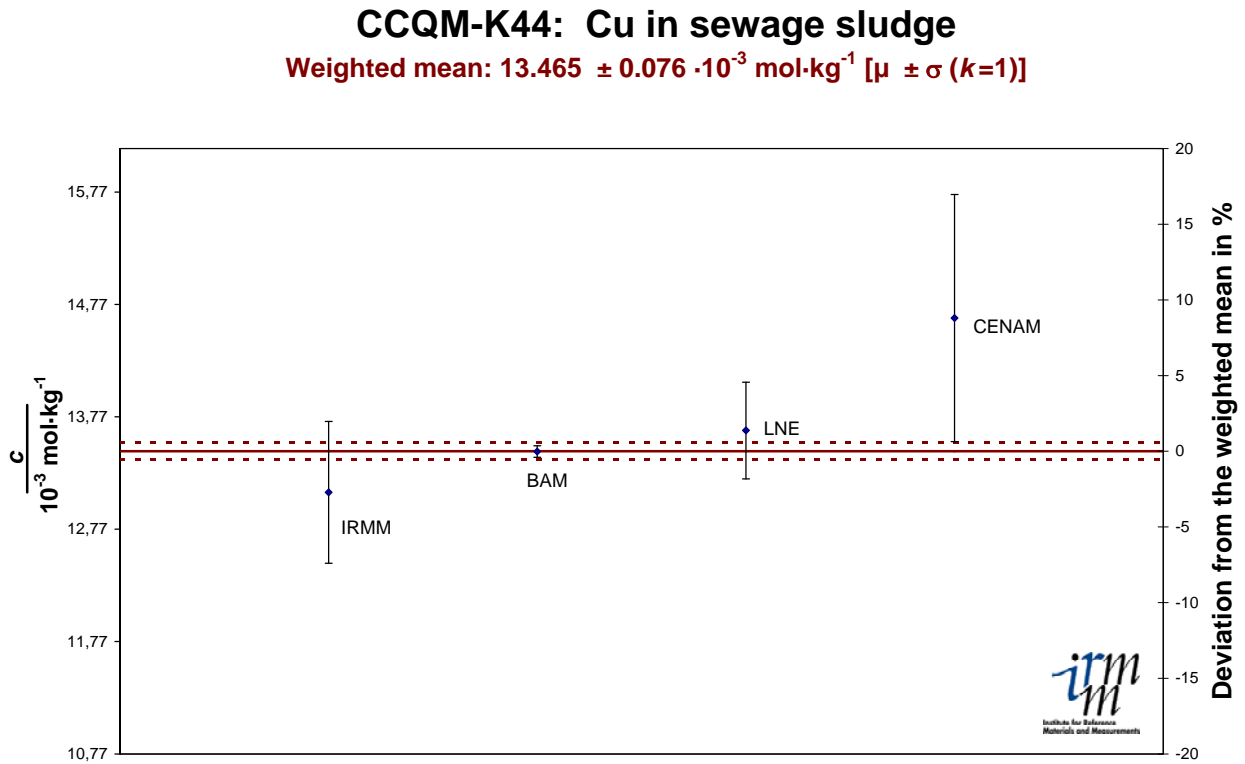


Figure 4

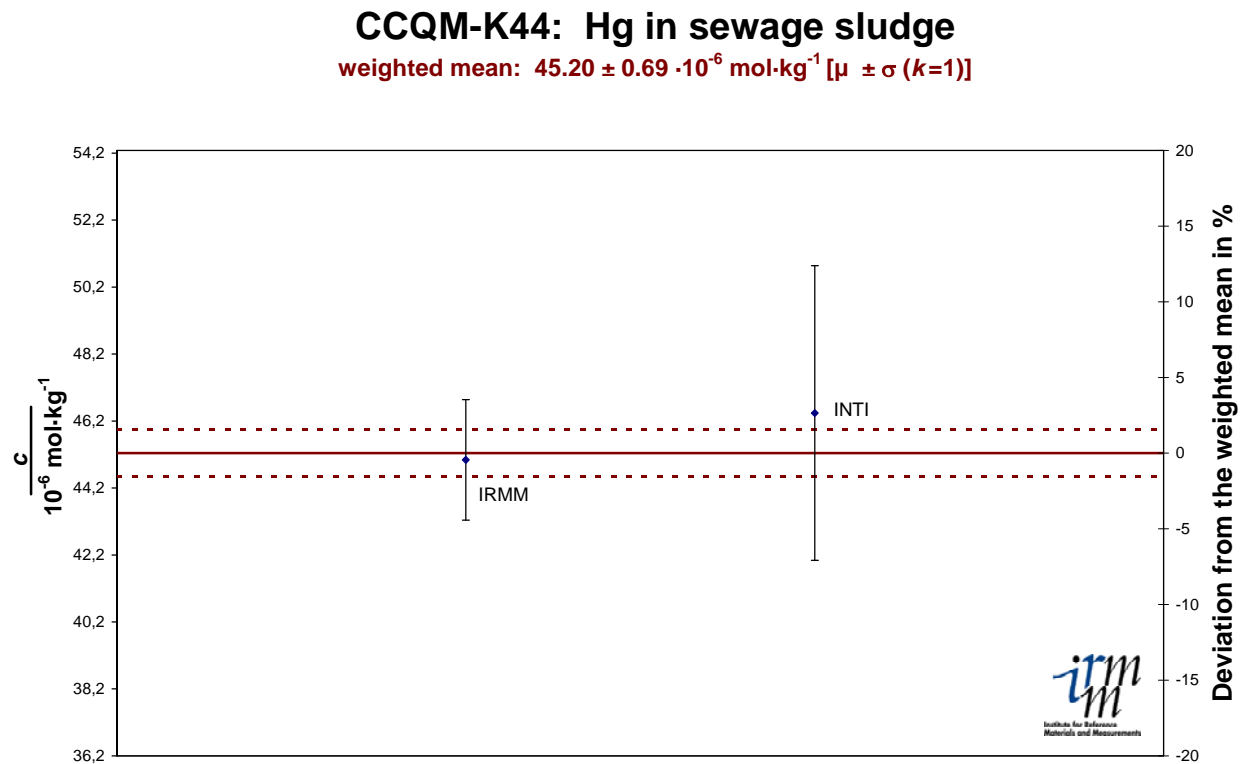


Figure 5

CCQM-K44: Ni in sewage sludge
inconclusive

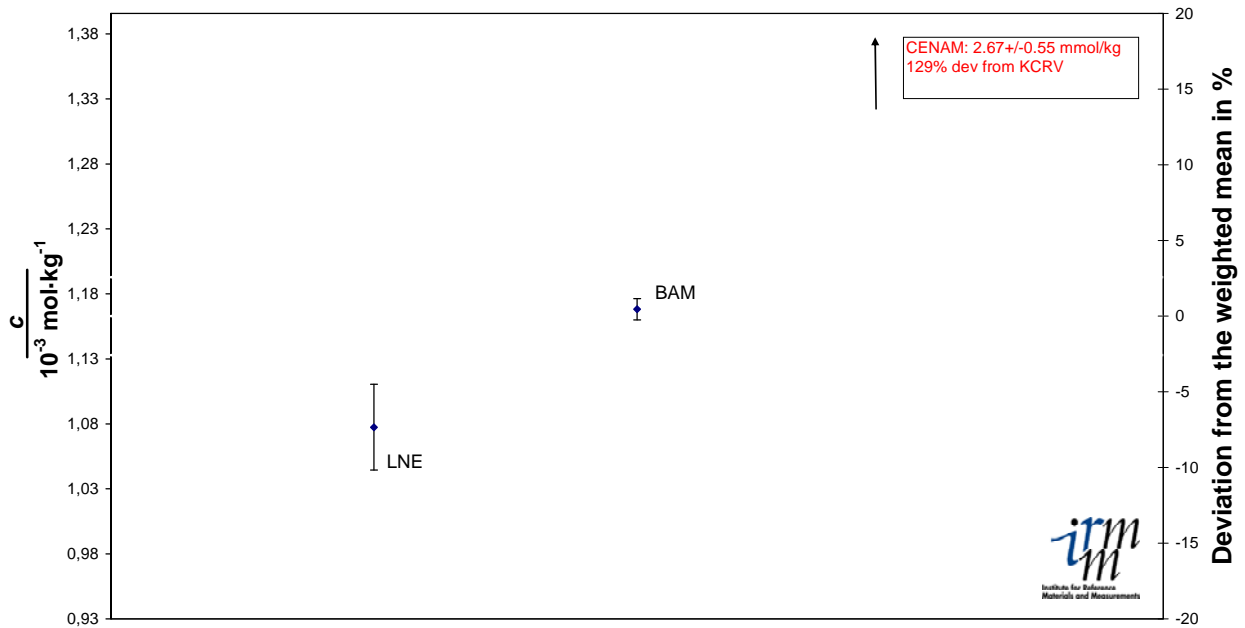


Figure 6

CCQM-K44: Pb in sewage sludge

Weighted mean with BAM_corrected: $2.964 \pm 0.092 \cdot 10^{-3} \text{ mol}\cdot\text{kg}^{-1} [\mu \pm \sigma (k=1)]$

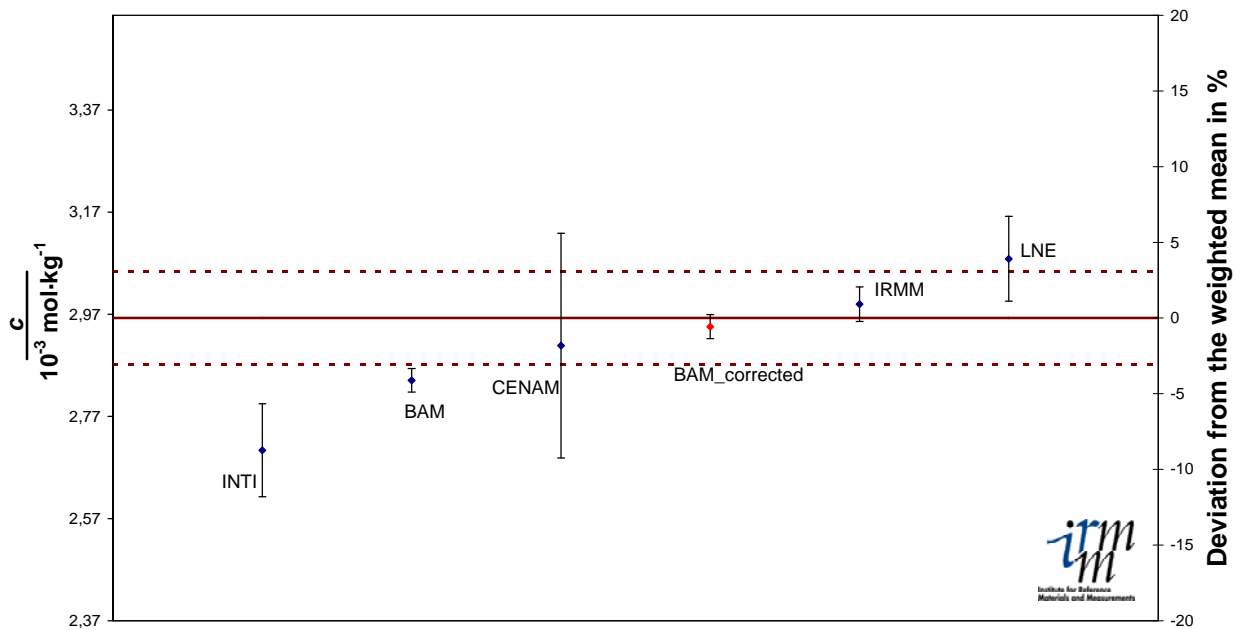
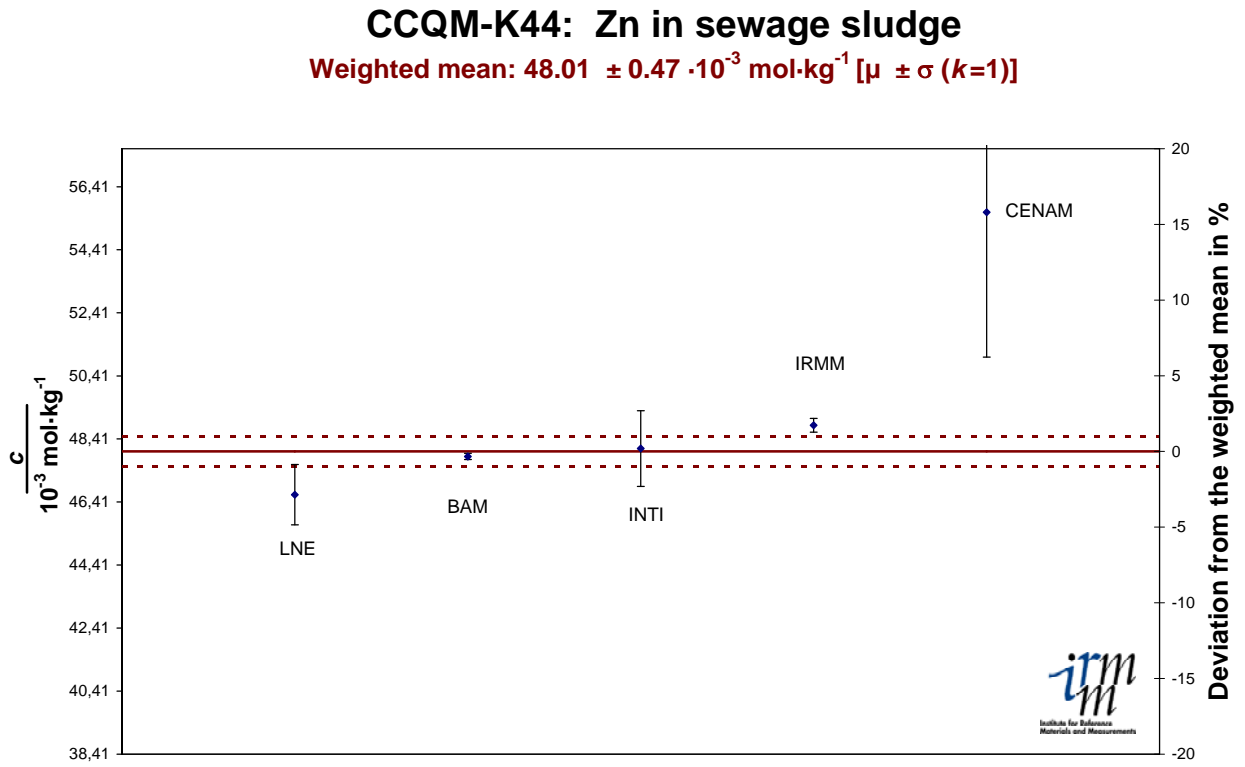


Figure 7



CCQM-K44: Trace Elements in Sewage Sludge

Annex 1 – All participants – Degree of equivalence

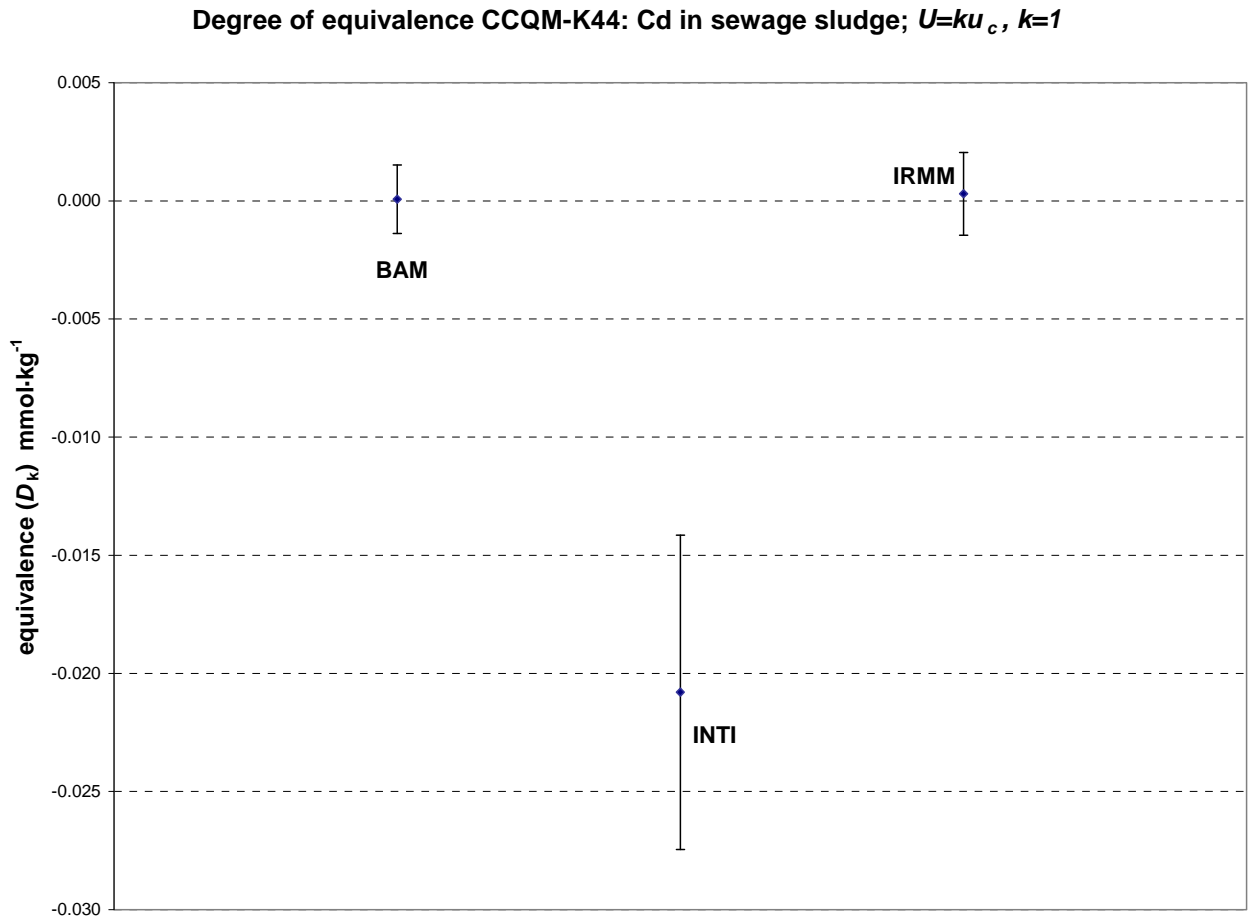
Figure	General Graphs	Page number
Figure 8	Degree of equivalence – Cd	21
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Figure 8 Degree of equivalence – Cd

Lab *i* ↓

	D_k	u_k
	mmol·kg ⁻¹	
BAM	0.0001	0.0014
INTI	-0.0208	0.0066
IRMM	0.0003	0.0018

Figure 9 Equivalence chart - Cd



CCQM- K44 Trace Elements in Sewage Sludge - Annex 1

Figure 10 Degree of equivalence – Cr

Lab *i* ↓

	D_k	u_k
	mmol·kg ⁻¹	
BAM	0.020	0.084
INTI	0.11	0.25
IRMM	0.17	0.12
LNE	-0.122	0.093

Figure 11 Equivalence chart - Cr

Degree of equivalence CCQM-K44: Cr in sewage sludge;
 $U=ku_c, k=1$

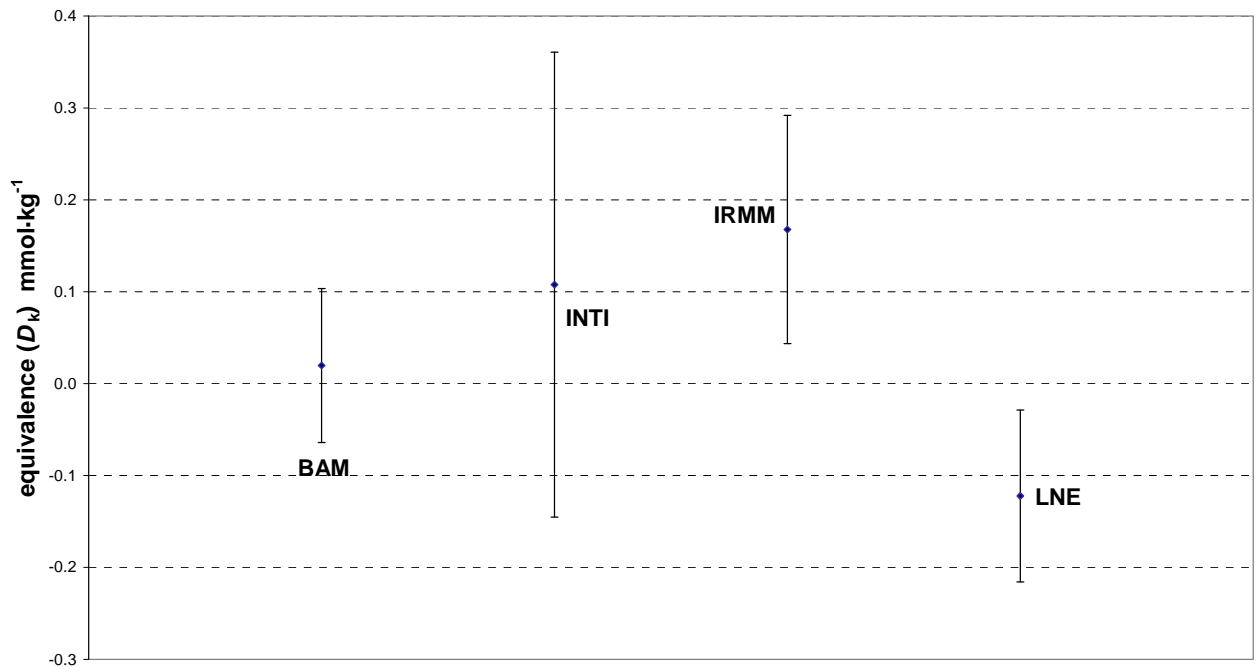
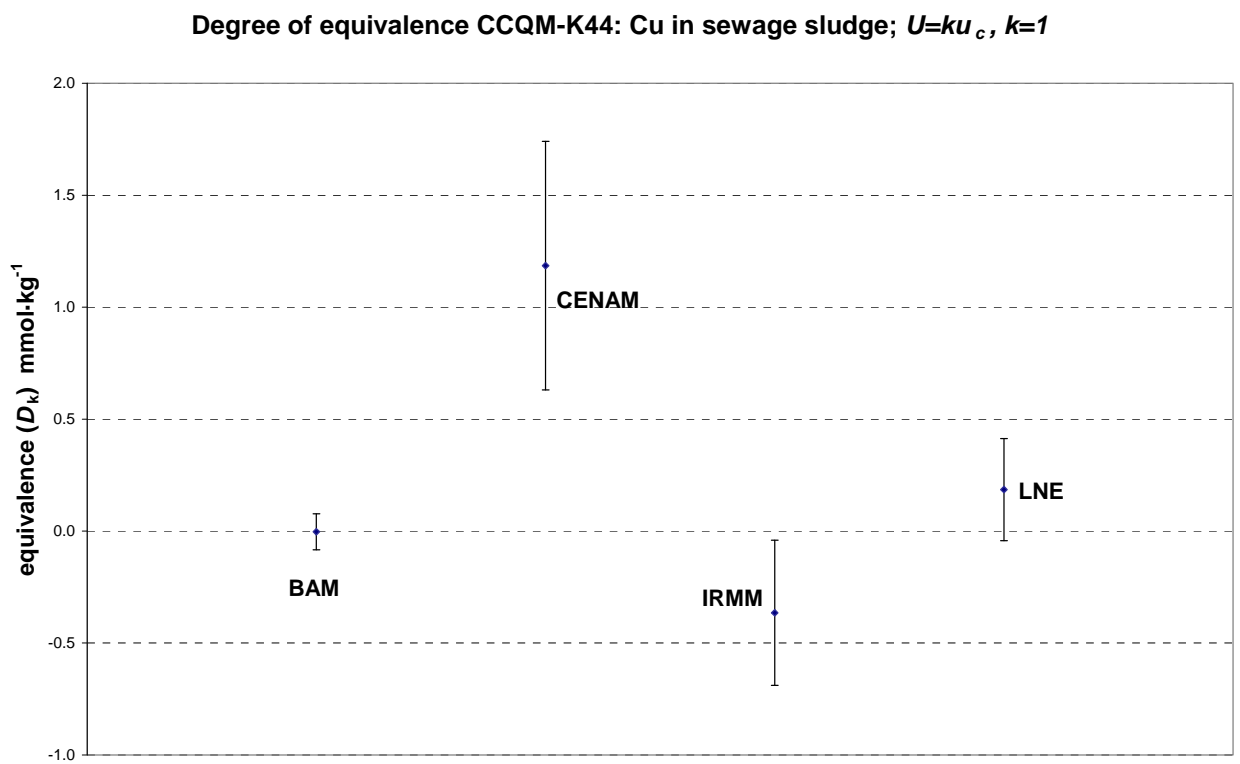


Figure 12 Degree of equivalence – Cu

Lab *i* ↓

	D_k	u_k
	mmol·kg ⁻¹	
BAM	-0.0030	0.0802
CENAM	1.19	0.56
IRMM	-0.37	0.32
LNE	0.19	0.23

Figure 13 Equivalence chart - Cu



CCQM- K44 Trace Elements in Sewage Sludge - Annex 1

Figure 14 Degree of equivalence – Hg

Lab <i>i</i>	D_k	u_k
	mmol·kg ⁻¹	
INTI	0.0012	0.0023
IRMM	-0.0002	0.0011

Figure 15 Equivalence chart - Hg

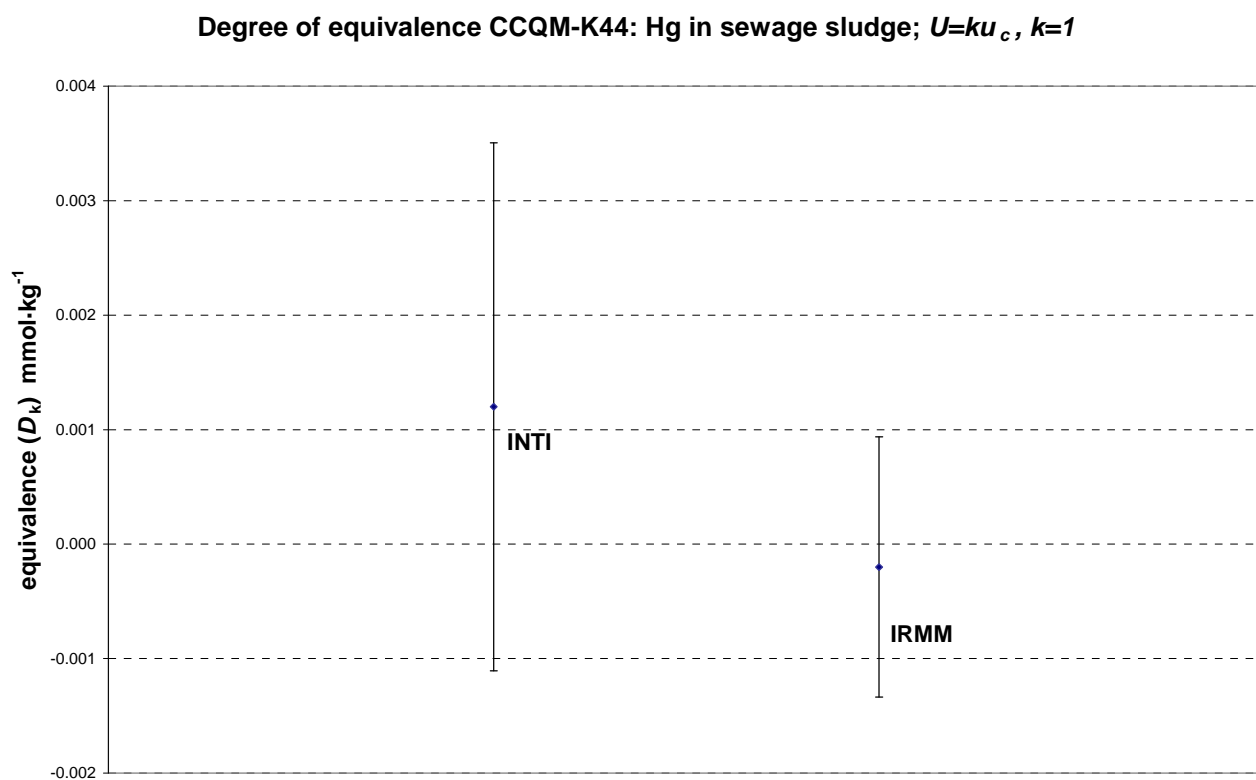


Figure 16 Inconclusive, no degree of equivalence for Ni

Figure 17 Inconclusive, no equivalence chart for Ni

CCQM- K44 Trace Elements in Sewage Sludge - Annex 1

Figure 18 Degree of equivalence – Pb

Lab *i* ↓

	D_k	u_k
	mmol·kg ⁻¹	
BAM	-0.122	0.093
CENAM	-0.05	0.14
INTI	-0.26	0.10
IRMM	0.027	0.093
LNE	0.12	0.10

Figure 19 Equivalence chart - Pb

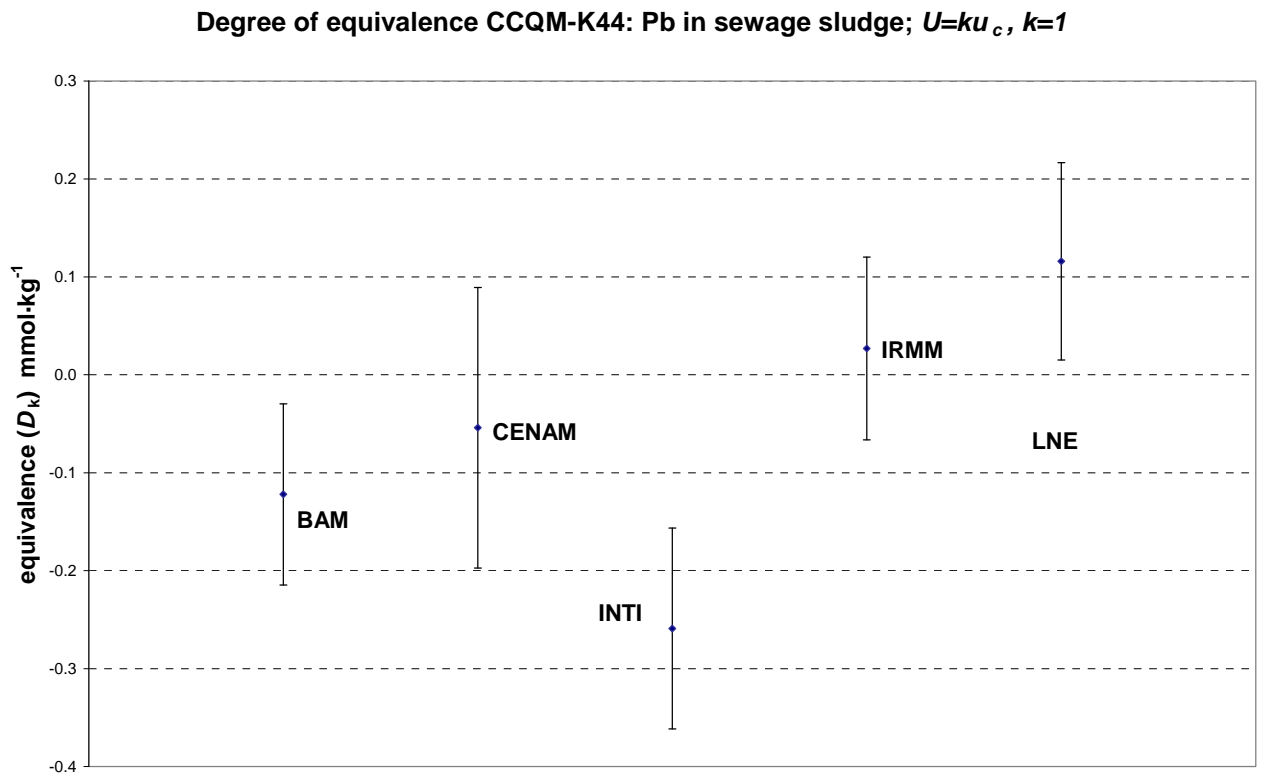


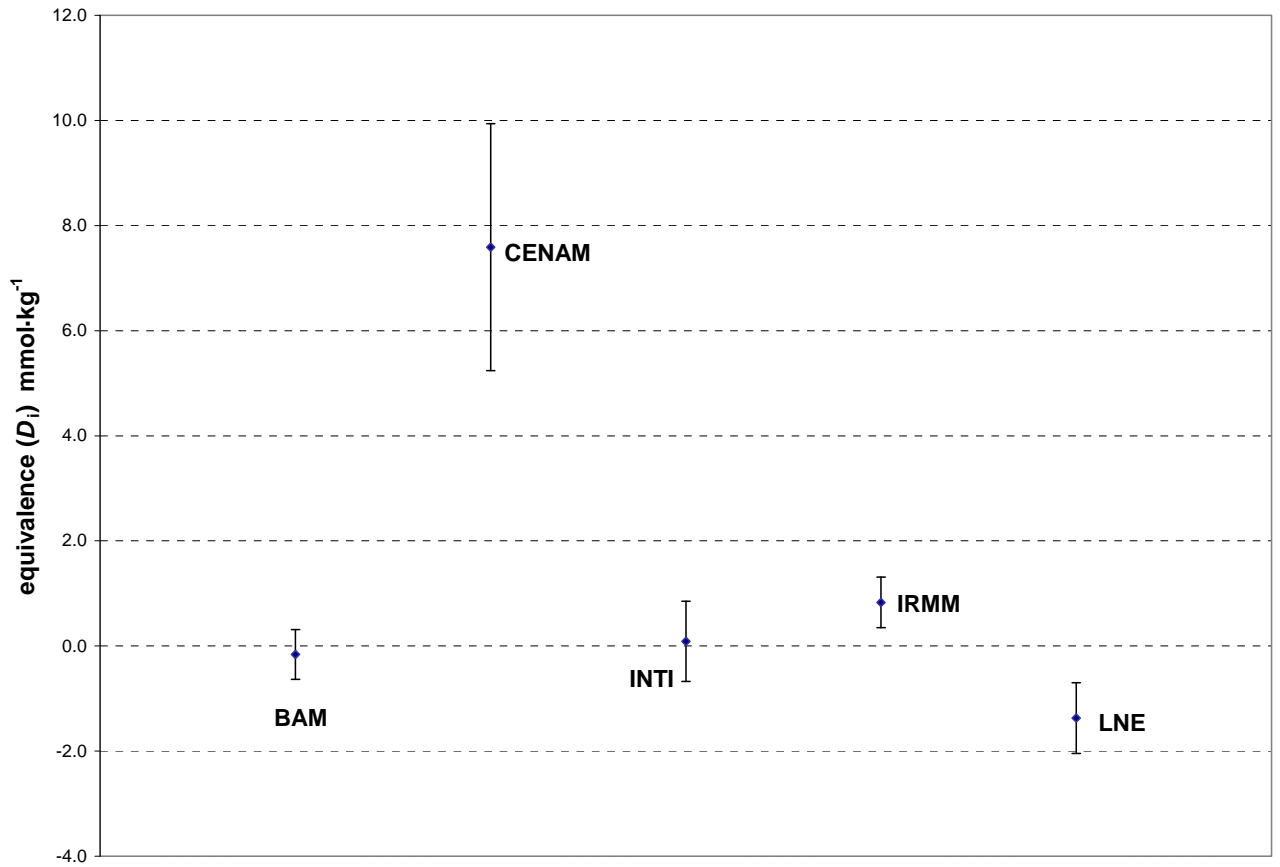
Figure 20 Degree of equivalence – Zn

Lab *i* ↓

	D_k	u_k
	mmol·kg ⁻¹	
BAM	-0.16	0.47
CENAM	7.59	2.35
INTI	0.09	0.76
IRMM	0.83	0.48
LNE	-1.37	0.67

Figure 21 Equivalence chart - Zn

Degree of equivalence CCQM-K44: Zn in sewage sludge; $U=ku_c$, $k=1$



Annex 2 – Questionnaire data

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CCQM-K44: Trace Elements in Sewage Sludge

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Questionnaire data	

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Annex 2 – Questionnaire data

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CCQM-K44 Trace Elements in Sewage Sludge - Annex 2

Table 1 Digestion method and acid mixture

REPORTED QUESTIONNAIRE DATA							
Participant	Cd	Cr	Cu	Hg	Ni	Pb	Zn
BAM	2-step MW digestion with HNO ₃ +H ₂ O ₂ + H ₂ O+ at 220°C	2-step MW digestion with HNO ₃ +H ₂ O ₂ + H ₂ O+ at 220°C	2-step MW digestion with HNO ₃ +H ₂ O ₂ + H ₂ O+ at 220°C	-	2-step MW digestion with HNO ₃ +H ₂ O ₂ + H ₂ O+ at 220°C	2-step MW digestion with HNO ₃ +H ₂ O ₂ + H ₂ O+ at 220°C	2-step MW digestion with HNO ₃ +H ₂ O ₂ + H ₂ O+ at 220°C
CENAM	-	-	Borate fusion	-	Borate fusion	Borate fusion	Borate fusion
EC-JRC-IRMM	-	-	-	Cold pre-digestion step (>4 hours) with mixture H ₂ O ₂ + HNO ₃ +HF followed by 2 steps MW oven digestion (incl. add HCl)	-	Cold pre-digestion step (>4 hours) with mixture H ₂ O ₂ + HNO ₃ +HF followed by 2 steps MW oven digestion	Cold pre-digestion step (>4 hours) with mixture H ₂ O ₂ + HNO ₃ +HF followed by 2 steps MW oven digestion
INTI	MW, high pressure, closed vessel, H ₂ O+ HNO ₃ +HF+ HCl	MW, high pressure, closed vessel, H ₂ O+ HNO ₃ +HF+ HCl	-	MW, high pressure, closed vessel, H ₂ O+ HNO ₃ + H ₂ O ₂	-	MW, high pressure, closed vessel, H ₂ O+ HNO ₃ +HF+ HCl	MW, high pressure, closed vessel, H ₂ O+ HNO ₃ +HF+ HCl
LNE	MW (5 ml HNO ₃ + 1 ml H ₂ O ₂ + 0.3 ml HF)	MW (5 ml HNO ₃ + 1 ml H ₂ O ₂ + 0.3 ml HF)	MW (5 ml HNO ₃ + 1 ml H ₂ O ₂ + 0.3 ml HF)	-	MW (5 ml HNO ₃ + 1 ml H ₂ O ₂ + 0.3 ml HF)	MW (5 ml HNO ₃ + 1 ml H ₂ O ₂ + 0.3 ml HF)	MW (5 ml HNO ₃ + 1 ml H ₂ O ₂ + 0.3 ml HF)

Table 2 Reference isotope for IDMS

REPORTED QUESTIONNAIRE DATA							
Participant	Cd	Cr	Cu	Hg	Ni	Pb	Zn
BAM	114/113	52/53	63/65	-	58/61	208/206	64/67
EC-JRC-IRMM	111	-	-	²⁰² Hg	-	²⁰⁶ Pb	⁶⁸ Zn
LNE	-	52/53	63/65	-	60/61	208/206	68/67

Table 3 Number of blends

REPORTED QUESTIONNAIRE DATA							
Participant	Cd	Cr	Cu	Hg	Ni	Pb	Zn
BAM	6	6	9	-	9	9	6
EC-JRCIRMM	15	-	-	15	-	15	10
LNE	-	6	6	-	6	4	6

Table 4 Experimental reproducibility

REPORTED QUESTIONNAIRE DATA							
Participant	Cd	Cr	Cu	Hg	Ni	Pb	Zn
BAM	0.21%	0.64%	0.13%	-	0.33%	0.39%	0.09%
EC-JRCIRMM	0.75%	-	-	3.1%	-	1.01%	0.38%
INTI	3.9%	0.6%	-	4.1%	-	1.6%	0.7%
IRMM_SCK	-	0.6%	2.5%	-	-	-	-
LNE	-	2.7%	2.7%	-	2.7%	1.5%	1.5%

CCQM-K44 Trace Elements in Sewage Sludge - Annex 2

Table 5 (Isotopic) reference materials used for calibration

REPORTED QUESTIONNAIRE DATA							
Participant	Cd	Cr	Cu	Hg	Ni	Pb	Zn
BAM	-	-	-	-	-	NBS 981	-
CENAM	-	-	-	-	-	-	-
EC-JRC-IRMM	Natural Cd solution with IUPAC values	-	-	IRMM-639	-	NBS 981	IRMM-3702
INTI	NIST SRM 3108	NIST SRM 3112 a	-	NIST SRM 1641 d.	-	NIST SRM 3128	NIST SRM 3168 a
IRMM_SCK	-	ICP Alfa Aesar Cr solution	ICP Alfa Aesar Cu solution	-	-	-	-
LNE	-	enriched Cr 53 solution (IRMM)	enriched Cu 65 solution (Spectrascan)	-	enriched Ni 61 solution (Spectrascan)	enriched Pb 206 solution (NIST)	enriched Zn 67 solution (Spectrascan)

Table 6 Use of square root of n for type A uncertainty contributions

REPORTED QUESTIONNAIRE DATA	
Participant	Sqrt (n)
BAM	No
CENAM	Yes
EC-JRC-IRMM	Yes
INTI	Yes
IRMM_SCK	Yes
LNE	Yes

