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PRACTITIONER'S REPORT

International comparison of the determination of cadmium and lead in herb: the Comité Consultatif pour la Quantité de Matière (CCQM) pilot study CCQM-P97

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Abstract A Comité Consultatif pour la Quantité de Matière (CCQM) inter-laboratory comparison program, CCQM-P97, for the analysis of cadmium and lead in *Herba Demodii Styracifolii* was organized by the Hong Kong Government Laboratory. The objective of the program was to establish comparability of trace metals analysis in herbal matrices amongst the participating national metrology institutes. The arithmetic mean values of the 13 participants were 0.3186 mg kg^{-1} (RSD = 11.3%) and 1.650 mg kg^{-1} (RSD = 11.0%) for cadmium and lead, respectively. The participants using double-isotope dilution mass spectrometry technique for their quantification were found to provide similar mean values to those of non-isotope dilution mass spectrometry users. The observation indicated that trace metal analysis in herbal matrices was not method-dependent, but the use of the highest metrological IDMS approach gave a better precision than other routine calibration methods.

Keywords Cadmium · Lead · Herb sample · CCQM · Inter-laboratory comparison

Introduction

Treatments with herbal medicines are commonly advocated for a wide range of conditions in many Asian countries and have recently become popular in the West [1]. However, the ubiquitous presence of heavy metals in the environment arising from various natural and anthropogenic activities has led to the intrusion of these substances into agricultural products including herbal plants. Hence, heavy metal contaminations are often regarded by legislators as one of the critical safety issues for addressing the judicious use of herbal materials, and we have seen extensive surveillance monitoring and laboratory testing of heavy metals in herbs being carried out worldwide now-a-days. Furthermore, a

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number of studies exposed the contamination problems in herbal plants and products [2–4]. Literature information revealed that cadmium and lead were mostly found in a wide variety of herbs and their concentrations were respectively in the range of 0.2–2.7 mg kg^{-1} for cadmium and 0.1–2.8 mg kg^{-1} for lead [5]. As a consequence, reliable and traceable measurement of these contaminants is essential for the safety evaluation and risk assessment that underpins the wider use of traditional and complementary medicinal herbs.

To promote and develop metrology in chemistry and help build a scientific infrastructure that supports the removal of technical barriers to trade and to benchmark the calibration and measurement capabilities amongst national metrology institutes and designated institutes, the Comité Consultatif pour la Quantité de Matière (CCQM) was established in 1993 (http://www.bipm.org). Amongst others, the CCQM coordinates inter-laboratory comparison programs under the auspices of the Comité International des Poids et Mesures Mutual Recognition Arrangement. Since its inception, the CCQM has organized over 180 intercomparisons in various areas within the chemical testing field. For instance, for inorganic measurements, a number of inter-laboratory comparisons on trace elements in sediment [6], wine [7], bovine liver [8], rice [9], and soybean [10] were organized.

In view of the growing global interest in traditional medicine and the absence of relevant inter-laboratory studies for the safety evaluation of herbs in respect of heavy metal contamination, a pilot study on the determination of cadmium and lead in *Herba Demodii Styracifolii* was proposed by the Hong Kong Government Laboratory at the Inorganic Analysis Working Group meeting of the CCQM in Beijing, China in October 2006. *Herba Desmodii Styracifolii*, which is one of Chinese herbal medicines regulated under Chapter 549, Chinese Medicine Ordinance of the laws of Hong Kong, is a popular herb used by the Chinese community with the indications of promoting diuresis and relieving stranguria. Some national metrology institutes' representatives showed their enthusiasm in joining the program at the meeting and the pilot study (CCQM-P97) was eventually approved by the IAWG Committee in early 2007. A call for participation was sent out to all national metrology institutes in May 2007, and samples were distributed to all registered participants in August 2007. The participants were requested to submit results to the coordinating laboratory by 31 December that year. Concurrently, a regional pilot study, APMP.QM-P10 using the same study material was approved to run in parallel with CCQM-P97 under the auspices of the Asia-Pacific Metrology Program Technical Committee on Amount of Substances for national metrology institutes in the Asia-Pacific region.

Materials and methods

Preparation of samples

Several batches of dried samples of *Herba Desmodii Styracifolii* were purchased from a local market after being authenticated by the organizer. The herbal materials were confirmed to contain trace quantities of incurred cadmium (ranging from 0.1 to 0.5 mg kg^{-1} level) and lead (ranging from 1 to 5 mg kg^{-1} level) and were rinsed with distilled water to remove dirt and foreign matters. The washed samples were air-dried in a Clean Room (Class 1000 specification), then subjected to freeze-drying, grinding, sieving (through 100 μm sieve), and thorough mixing. Aliquots of about 5 g of the well-mixed fine powder were packaged into pre-cleaned and nitrogen-flushed amber glass bottles. The bottles were sterilized with γ-irradiation at about 1 kGy to prevent microbial growth, and were vacuum-sealed in polypropylene bags. More than 300 bottles of herbal samples were prepared and stored at room temperature before shipment.

Homogeneity and stability studies

Seventeen bottles were randomly taken for within- and between-bottle homogeneity study. Two aliquots of 0.5 g from each sample bottle was analyzed using a validated inductively coupled plasma-mass spectrometry method as described in the Analytical method section below. The analysis of the 34 duplicate samples was arranged in a randomized order, and the analysis was completed within the shortest time possible to minimize errors arising from instrumental bias. The overall sample homogeneity was assessed by a one-way analysis of variance (ANOVA). The degree of sample homogeneity should be such that differences between sample batches would not significantly affect the evaluation of participants' results.

The stability of samples was assessed by analysis sample bottles that had been stored at 37 °C and room temperature (25 °C). Triplicate portions were taken at the 1, 2, and 12-month intervals from samples stored at both temperatures. The relative standard deviations of results were determined and the mass fractions were tested by regression analysis.

Analytical method for homogeneity and stability studies

An accurate weighed aliquot of about 0.5 g was placed into a Teflon digestion vessel and 10 mL of concentrated nitric acid (70% by mass, Tracemetal grade) was added. The vessel was sealed and positioned into the turntable in a microwave system with a maximum power of 1200 W. The microwave-assisted digestion program was operated at full power at 1.4×10^5 N m^{-2} and 75 °C, held for 1 min, and then gradually ramped to 3.5×10^5 N m^{-2} and 180 °C. The vessel was then cooled until the temperature fell below 50 °C or pressure below 3.5×10^4 N m^{-2} at the end of the digestion program. The digestion vessel in the turntable was taken to a fume hood and vented manually with caution. The digested sample solution was transferred to a 50 mL volumetric flask and made up to the volume with distilled water. A correction blank was prepared in the same way as the procedure described above. An appropriate volume of the diluted digested solution and an aliquot of 0.1 mL of the intermediate internal standard solution were added into a 15 mL graduated disposable plastic tube. The intermediate internal standard solution was prepared by adding 100 µL of 1 000 mg L^{-1} of standard stock solutions of germanium (Ge) and indium (In) to a 200 mL volumetric flask and made up to volume with 1% nitric acid (v/v). The final mass concentrations of Ge and In in the diluted sample solution should be about 5 µg L^{-1}. A series of mixed working calibration standard solutions with appropriate mass concentration ranges was used for quantification of analytes in the sample. The conditions of inductively coupled plasma-mass spectrometry were optimized and operated in accordance with the manufacturer's manual. Isotopes of ^{111}Cd, ^{114}Cd, ^{206}Pb, ^{207}Pb, and ^{208}Pb were monitored to counter-check for the presence of spectral interferences. The mass fractions (w) of cadmium and lead in mg kg^{-1} were calculated using the equation as follows:

$$w = (cD - B)V/m \qquad (1)$$

where c is the mass concentration (µg L^{-1}) of analyte in the working sample solution; D is the dilution factor of 1 in this experiment; B is the mass concentration (µg L^{-1}) of analyte in the digestion blank; V is the volume (L) of sample solution made up after digestion and m is the mass (kg) of the sample used.

Protocol

Participants in the CCQM-P97 were provided with three bottles (one bottle for a trial run and two bottles for data reporting) each of about 5 g of herbal powder containing incurred cadmium and lead at the mg kg^{-1} level. To avoid contamination and possible degradation, the sample bottles were tightly capped and any exposure to direct light avoided. Participants should use their preferred methodology to analyze the sample, with a recommended sample size of at least 0.1 g, and to report dry mass fractions of the measurands in mg kg^{-1} for each bottle unit and the combined mean value of the two bottle units on the result sheet provided. Since moisture content could be dependent upon the method being used and would significantly affect the values for dry mass correction, the determined moisture content was then used to correct values for dry mass data. Participants were recommended to take a minimum of three portions (with a recommended size of 0.5 g each) of the sample and place over the anhydrous calcium sulfate (e.g. Drierite) in a desiccator at room temperature for a minimum of 10 days until a constant mass was reached.

Participants were also requested to provide the detailed technical information such as the analytical method of measurement; source and purity of any reference and/or standard materials used and full measurement uncertainty including all potential uncertainty components; combined standard uncertainty; expanded uncertainty and the coverage factor.

Results and discussion

Homogeneity and stability studies

The average mass fraction, not corrected for dry mass, of cadmium and lead from the 34 results in the homogeneity study were 0.263 mg kg^{-1} (RSD = 1.5%) and 1.463 mg kg^{-1} (RSD = 1.7%), respectively. One-way ANOVA showed that the F_{test} values (1.452 for cadmium and 1.950 for lead, respectively) were smaller than the F_{critical} (2.289 at 95% confidence interval with a degree of freedom = 33). The degree of homogeneity demonstrated for the sample prepared was satisfactory and should be appropriate to be used in the inter-laboratory comparison program. The stability of samples was conducted by analysis of portions of some randomly selected sample bottles that had been stored at 25 and 37 °C over a 12-month period. It was found that the percent deviation of cadmium varied from −1.4 to 2.3% and lead from −2.6 to 3.0%, respectively. The RSD of both measurands ranged from 1.7 to 2.4% at 25 °C and from 1.0 to 1.4% at 37 °C, respectively. There was no significant change in the mass fraction of cadmium and lead over the 12-month when tested by regression analysis. The results of the above statistical treatments indicated that cadmium and lead in the sample were stable at an elevated temperature of 37 °C for at least 1 year and were expected to be stable for a longer time when the samples are kept at room temperature.

Participating laboratories and methods used

A breakdown of the 14 laboratories (7 Asian, 3 American, 3 European and 1 international) that registered for the CCQM-P97 pilot study was tabulated in Table 1. All participants are either national metrology institutes or designated institutes under the Comité International des

Table 1 List of CCQM-P97 participating laboratories

Participant	Acronym	Origin
Instituto Nacional de Technologia Industrial	INTI	Argentina
International Atomic Energy Agency	IAEA	Austria
National Centre of Metrology, Bulgaria	BIM	Bulgaria
National Institute of Metrology, China	NIM	China
Laboratoire National de Métrologie et d'essais	LNE	France
Government Laboratory, Hong Kong	HKGL	Hong Kong
National Physical Laboratory, India	NPLI	India
Indonesian Institute of Sciences	LIPI	Indonesia
Korea Research Institute of Standards and Sciences	KRISS	Korea
Health Sciences Authority	HSA	Singapore
National Institute of Metrology, Thailand	NIMT	Thailand
Tubitak National Metrology Institute	UME	Turkey
National Institute of Standards and Technology	NIST	USA
Laboratorio Tecnologico de Uruguay	LATU	Uruguay

Poids et Mesures Mutual Recognition Arrangement. Eleven participants returned their results on time (before 31 December 2007), and two requested, with the permission from the organizer, for an extension of about 2 weeks (18 January 2008) due to the failure of instruments. One participant did not report.

The sample digestion used by all participants relied on the microwave assisted method with either concentrated nitric acid or different mixtures of nitric acid with hydrogen peroxide, hydrochloric acid and/or hydrofluoric acid. Microwave digestion was reported to be one of the favorable methods for the digestion of foodstuff samples as complete digestion can be affirmed in a relatively short time with minimal contamination as well as loss of analytes [11]. To achieve a total dissolution of cellulose-containing materials such as plant and grains, the application of the digestion medium consisting of nitric acid and hydrogen peroxide [12, 13] or nitric acid and hydrofluoric acid [14] was found to be effective. On the basis of the given information, it would be expected that the microwave-assisted acid digestion used by participants was an adequate sample pre-treatment method for the test material prior to the instrumental analysis.

The analyses of cadmium and lead were carried out using flame atomic absorption spectrometry, graphite furnace atomic absorption spectrometry or inductively coupled plasma-mass spectrometry. These are the common techniques to determine trace metals in environmental, biological, and agricultural samples. One participant used high resolution inductively coupled plasma-mass spectrometry. Six inductively coupled plasma-mass spectrometry users employed a double-isotope dilution mass spectrometry technique for their quantification; and the others used either external calibration or standard addition methods. A summary of participants' methodologies is tabulated in Table 2.

Participants' reported results

The results from the participating laboratories for cadmium and lead were summarized in Table 3 and graphically displayed in Fig. 1; 13 laboratories reported for cadmium and 12 for lead. Apart from one result on the analysis of lead by Lab. 9, all the mean values reported were derived from three (a minimum recommended) to ten determinations. Moisture

Table 2 Summary of methodologies used by participating laboratories

Participant code	Sample used (g)	Microwave digestion medium	Instrumentation	Quantification method
1	Not reported	$HNO_3 + H_2O_2$	FAAS	External calibration
2	0.5	5 mL HNO_3 + 1 mL H_2O_2	ICP-MS	External calibration
3	0.18	$HNO_3 + H_2O_2 + HF$	ICP-MS	Double IDMS
4	0.1	5 mL HNO_3 + 1 mL H_2O_2 + 0.2 mL HF	ICP-MS	Double IDMS
5	0.27	HNO_3 + HF	ICP-MS	Double IDMS
6	Not reported	10 mL HNO_3 + 2 mL H_2O_2	GFAAS	External calibration
7	0.5	$HNO_3 + H_2O_2$	GFAAS	Standard addition
8	Not reported	8 mL HNO_3 + 2 mL H_2O_2 + 2 mL HF	ICP-MS	Double IDMS
9	0.5	7 mL HNO_3	ICP-MS	External calibration
10	0.26	5 mL HNO_3 + 1 mL H_2O_2	ICP-MS	Double IDMS
11	0.5	7 mL HNO_3 + 2 mL H_2O_2	HR-ICP-MS	Standard addition
12	0.1	6 g HNO_3 + 1 g HF	ICP-MS	Double IDMS
13	0.37	5 mL HNO_3 + 1 mL HCl + 2 mL H_2O_2	GFAAS	Standard addition

FAAS flame atomic absorption spectrometry, *GFAAS* graphite furnace atomic absorption spectrometry, *ICP-MS* inductively coupled plasma-mass spectrometry, *HR-ICP-MS* high resolution inductively coupled plasma-mass spectrometry and *IDMS* isotope dilution mass spectrometry

Table 3 Reported results and uncertainty values for cadmium and lead (italic)

Participant Code	No. of Determination	Mean Mass Fraction ($\mathrm{mg\ kg^{-1}}$)	Expanded Uncertainty ($\mathrm{mg\ kg^{-1}}$)	Relative Expanded Uncertainty (%)	Coverage Factor (k)
1	6	0.387	0.014	3.6	2
	6	*2.035*	*0.052*	*2.6*	*2*
2	6	0.304	0.020	6.6	2
	6	*1.613*	*0.054*	*3.3*	*2*
3	6	0.3128	0.0056	1.8	2
	6	*1.557*	*0.040*	*2.6*	*2*
4	6	0.308	0.008	2.6	2
	6	*1.600*	*0.044*	*2.8*	*2*
5	4	0.3058	0.0074	2.4	2
	3	*1.6530*	*0.0249*	*1.5*	*2*
6	6	0.275	0.039	14.2	2
	4	*1.261*	*0.082*	*6.5*	*2*
7	6	0.347	0.023	6.6	2
	6	*1.85*	*0.30*	*16.2*	*2*
8	10	0.3141	0.0117	3.7	1.96
	10	*1.619*	*0.018*	*1.1*	*2.06*
9	4	0.25	0.04	16.0	2
	2	*1.59*	*0.38*	*23.9*	*2*
10	10	0.366	0.018	4.9	2
	10	*1.638*	*0.030*	*1.8*	*2*
11	6	0.318	0.006	1.9	2
	6	*1.71*	*0.04*	*2.3*	*2*
12	6	0.3094	0.0062	2.0	2
	6	*1.672*	*0.020*	*1.2*	*2*
13	3	0.345	0.015	4.3	2

content reported for dry mass correction ranged from 7.38 to 8.55%. Several participants used relevant types of matrix certified reference materials as one of their quality control protocols for validating the measurement: Lab 7 used NIES CRM 10b (rice powder) for cadmium and SRM 1575 (pine leaves) for lead; Lab 3 used SRM 1517a (pine needles) for cadmium and SRM 3246 (Ginkgo biloba leaves) for lead; Lab 12 used SRM 3240 (*Ephedra sinica* Stapf serial parts) for cadmium and SRM 3246 for lead; Lab 9 used GBW 07604 (poplar leaf); UME used SRM 1573a (tomato leaf) for cadmium. The reported mean values of cadmium ranged from 0.25 to 0.387 $\mathrm{mg\ kg^{-1}}$ and those of lead from 1.261 to 2.035 $\mathrm{mg\ kg^{-1}}$, respectively. As shown in Table 4, assigned values and their RSD using arithmetic mean, median, weighted mean and robust mean of the data were determined. Arithmetic mean values were found to be 0.3186 $\mathrm{mg\ kg^{-1}}$ (RSD = 11.3%) and 1.650 $\mathrm{mg\ kg^{-1}}$ (RSD = 11.0%) for cadmium and lead, respectively, and depicted no significant difference from those of other statistical calculations. Arithmetic mean values are used as the assigned values in this program because it is the simplest and direct way to express the average values and dispersions of the results of the participants. The spread of data in this program was larger than the results of cadmium in rice in the CCQM-P29 and trace metals in soybean in the CCQM-P64.

Uncertainty estimation

All participants reported the expanded uncertainty values and calculated using a coverage factor (k) at 2 or close to 2. The relative expanded uncertainties ranged from 1.8 to 16.0% (mean = 5.4%) for cadmium and 1.1 to 23.9% (mean = 5.5%) for lead, respectively. All participants provided explicit estimates of contribution to the dominant uncertainty that arose from their measurements. Regardless of the analytical techniques being used, precision (or repeatability/reproducibility) of replicate analysis was claimed to be the major uncertainty component by most of the participants, which were followed by dry mass correction and purity of stock standards (Table 5). The results from Lab 6 (cadmium only) and Lab 9 using external calibration and from Lab 7 (lead only) using standard addition showed their relative expanded uncertainties

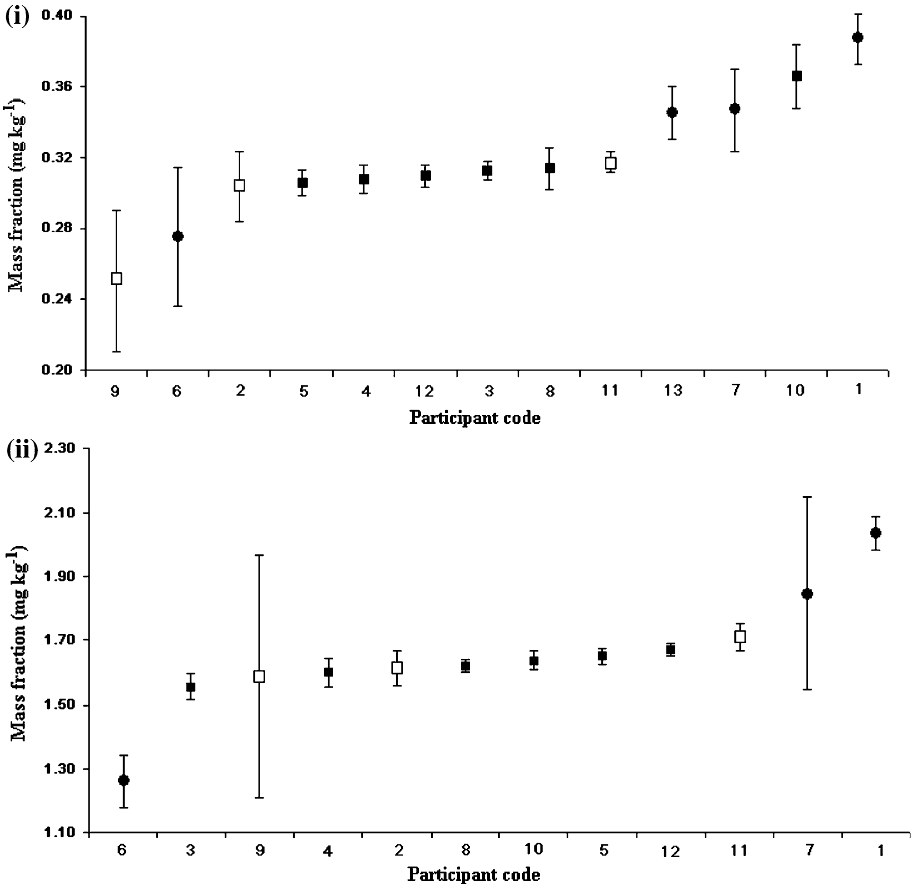

Fig. 1 Graphical illustration of results for (**i**) cadmium and (**ii**) lead. *Error bars* are the expanded uncertainties. *Circles* represents data were analysed by flame atomic absorption spectrometry or graphite furnace atomic absorption spectrometry, *open squares* inductively coupled plasma-mass spectrometry and *filled squares* inductively coupled plasma-isotope dilution mass spectrometry

Table 4 Statistical evaluation of the assigned values for cadmium and lead

	Cadmium		Lead	
	Mean mass fraction ± SD (mg kg^{-1})	RSD (%)	Mean mass fraction ± SD (mg kg^{-1})	RSD (%)
Arithmetic Mean	0.3186 ± 0.0361	11.3	1.650 ± 0.181	11.0
Median	0.3128 ± 0.0088	2.8	1.628 ± 0.041	2.5
Weighted Mean	0.3164 ± 0.0197	8.5	1.648 ± 0.100	6.1
Robust Mean	0.3186 ± 0.0346	10.9	1.642 ± 0.089	5.4

greater than 14%. On other hand, participants using the double-isotope dilution mass spectrometry technique (Labs 3, 4, 5, 8, 10 and 12) were found to report smaller expanded uncertainty values (1.8 to 4.9% for cadmium and 1.1 to 2.8% for lead, respectively) than those of other methods (1.9 to 16.0% for cadmium and 2.3 to 23.9% for lead, respectively). The fundamental principle of isotope dilution mass spectrometry that deals with the initial addition of a known amount of an isotopically labeled analog to the sample (or called the "sample blend") and to the blank (the "calibration blend") is straightforward. Isotope dilution mass spectrometry is traceable to SI unit and could be considered as a potentially primary method of analysis to inorganic and organic analyses [15] when the technique is cautiously applied. In addition, isotope dilution mass spectrometry provides clearly definable uncertainty budget estimation and is commonly used by national metrology institutes for certification of reference materials [16] and to provide accurate and precise measurements in the CCQM inter-laboratory comparison studies [17, 18]. There was no significant difference between the mean values generated from the isotope dilution mass spectrometry (1.6232 mg kg^{-1} for cadmium and 0.3194 mg kg^{-1} for lead) and non-isotope dilution mass spectrometry users (1.6765 mg kg^{-1} for cadmium and 0.3184 mg kg^{-1} for lead). However, isotope dilution mass spectrometry values are found to be more precise, in terms of the RSD, and the technique offers a higher metrological traceability than the others (Fig. 2). The RSDs of isotope dilution mass spectrometry were at 7.2 and 2.5% with respect to 14.6 and

Table 5 Summary of major uncertainties of participants

Participant Code	Major errors (in descending order)
1	Precision of method, volumetric dilutions, mass fraction of CRM, mass of samples
2	Precision of replicate analysis, recovery, dry mass correction
3	Precision of isotope ratios in samples and spikes, dry mass correction, mass fractions of standards
4	Precision of isotope ratios in samples and spikes, mass of samples, water content
5	Precision of isotope ratios in samples and spikes, mass bias correction factors, dry mass correction
6	Precision of replicate analysis, purity of stock standards
7	Repeatability of analysis, calibration curves, recovery, mass of samples
8	Precision of isotope ratios in samples and spikes, assay standards, dry mass correction
9	Precision of replicate analysis, purity of standards
10	Precision of isotope ratios in samples and spikes, digestion blank correction, purity of standards
11	Calibration curves, volumetric dilutions, repeatability of analysis, purity of standards
12	Interference correction (for cadmium only), dry mass correction, isotope ratio measurement factors, calibrant purity and preparation
13	Reproducibility of analysis, calibration standards, mass of samples

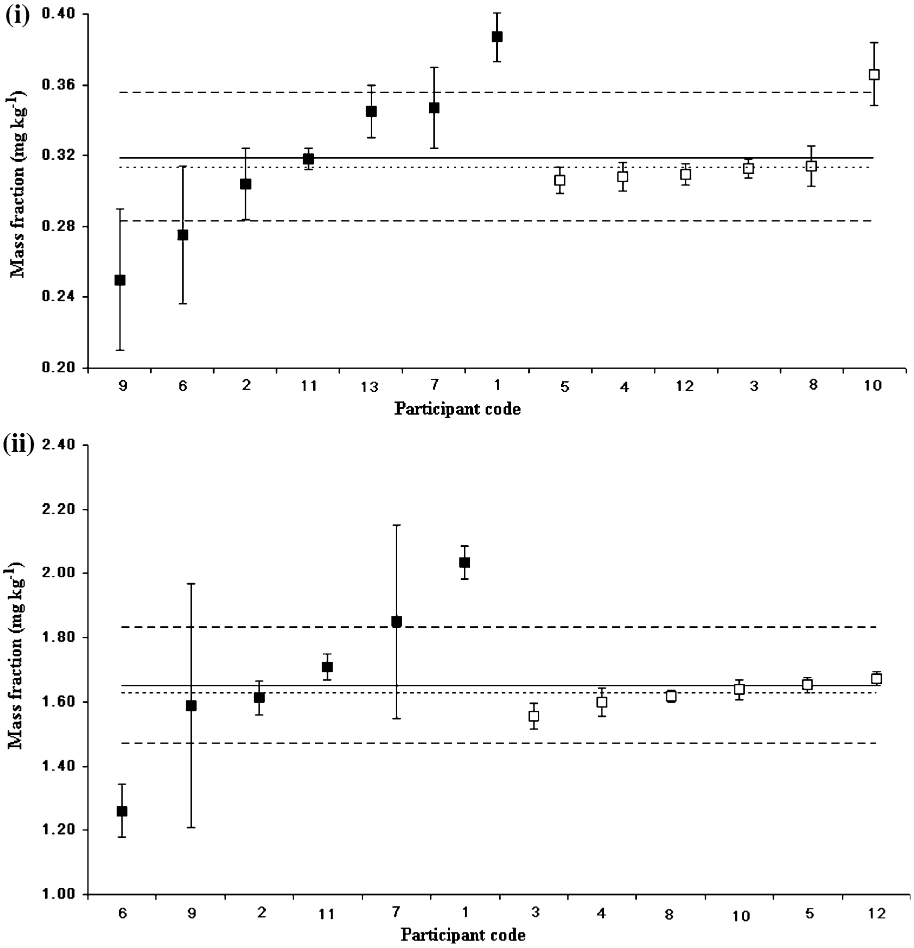

Fig. 2 Results for (**i**) cadmium and (**ii**) lead from non-isotope dilution mass spectrometry (*filled square*) and isotope dilution mass spectrometry (*open square*) users. *Dotted line* represents the median, and *solid line* represents the mean value with 1 SD as the upper and lower boundaries

15.6% for cadmium and lead, respectively. Given the expertise of the participating institutes, it is not surprising to note that the findings suggest that the measurement results are not method-dependent for the concerned measurements of inorganic measurements of inorganic analytes in herbal matrices but the skill and experience of the analysts are more important than the type of instrumental and calibration technique being employed.

Conclusions

Concerning the analytical techniques being used, there is no significant difference for the mean results obtained by isotope dilution mass spectrometry than those of standard addition and external calibration methods. However, isotope dilution mass spectrometry values are found to be more precise, in terms of the RSD, and the technique offers a higher traceability than others. In addition, laboratories using isotope dilution mass spectrometry gave smaller relative uncertainty values when compared with those of non-isotope dilution mass spectrometry users.

The overall performance of the program is fairly satisfactory and the majority of the participants are able to quantify incurred cadmium and lead in herbal material within the expected target mass fraction ranges. Without eliminating any of the submitted data, the dispersion of the results, in terms of the RSD for both analytes is about 11%. On the basis of good agreements of results for arithmetic means, median, weighted means, and robust means, the arithmetic means are recommended to be used as the assigned values for the tested sample in the program.

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