

Accurate Quantification of Cadmium, Chromium, Mercury and Lead in Plastics for RoHS Compliance using the Agilent 7500ce ICP-MS

Application note

Environmental

Author

Sarah Hill and
Rebeca Santamaria-Fernandez
LGC Ltd.
Queens Road
Teddington, Middlesex, TW11 0LY
UK

Abstract

This application note describes the quantification of cadmium, chromium, lead and mercury in plastic materials by external calibration using the Agilent 7500ce ICP-MS system equipped with an Octopole Reaction System (ORS). Isotope dilution analysis with ICP-MS was used as a confirmatory technique. Good agreement of the results obtained by the two calibration approaches was achieved. The sample digestion methodology, tuning considerations, results and uncertainty estimations are discussed. The method validated with IDMS results has potential as a fast analytical tool for compliance testing laboratories.



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Introduction

The Restriction of Hazardous Substances (RoHS) Directive (2002/95/EC) became influential in 2006 and places restrictions on the maximum allowable quantity of cadmium (0.01%), hexavalent chromium (0.1%), lead (0.1%) and mercury (0.1%) in all new electrical and electronic equipment [1]. The implementation of this recent EU legislation and public concern over the potential for toxic elements to be present in imported toys has put the heavy metal content of plastics into the limelight.

Several other countries such as China, Japan and some states in the USA have followed the EU's lead and have introduced similar legislation. In order to facilitate international trade, there is the need for accurate methods of quantification for these regulated elements to enable importing and exporting across borders. Such methods will also help ensure that goods comply with written specifications and legal requirements. The capability of making comparable measurements in different countries is necessary to remove any technical barrier to international trade.

In order to achieve this recognition of comparable measurements, National Metrology Institutes (NMIs) and designated laboratories participate in comparison studies to prove their capabilities and to provide traceability to the International System of Units (SI). NMIs and associated reference laboratories provide links to the SI for field laboratories through the availability of certified reference materials (CRMs), calibration standards and other calibration services such as reference values for proficiency testing or quality assurance schemes.

In this work, an Agilent 7500ce ICP-MS has been used for the accurate quantification of chromium, cadmium, mercury and lead in plastics by external calibration following microwave acid sample digestion. Confirmation values have been obtained by isotope dilution mass spectrometry (IDMS), a highly accurate and precise method which is traceable to the SI. The results obtained by IDMS were used to validate the external calibration method, which can then be used by field laboratories. The uncertainty associated with the results of both approaches was estimated according to ISO/GUM [2] and Eurachem/CITAC [3] guidelines. Furthermore, the IDMS results were used in an international interlaboratory comparison exercise, where excellent agreement was found between the participants.

Experimental

Standards and Reagents

High purity primary standards were used for both external calibration and IDMS, specifically: Cr NIST SRM 3112a, Cd NIST SRM 3108, Hg NIST SRM 3133 and Pb NIST SRM 981 (National Institute of Standards and Technology, Gaithersburg, USA). They were used to prepare a multi-element stock standard solution in 6% nitric acid (Aristar®, BDH, UK), which was diluted appropriately and used for both calibration methods, as subsequently described. All work was performed gravimetrically to ensure maximum accuracy. For external calibration, the multi-element standard stock solution containing 999.6 ng/g Cr, 74.9 ng/g Cd, 250.0 ng/g Hg and 1101.4 ng/g Pb in nitric acid was diluted to give three calibration standards plus a blank which covered the expected range for the samples and CRMs. No problems with the stability of Hg in standard nitric acid solutions were observed over the time of the study. Calibration standards were prepared from the main stock solution on the day of analysis. Moreover, sample digests were measured within a week of preparation to minimize the effect of any potential losses.

Quality Control

In order to assess the accuracy of the methodology, two plastic (polyethylene) CRMs were used in this work, namely BCR 680 and ERM EC681k (LGC Standards, UK). The certified values and the expanded uncertainties for these materials are given in Table 1. Additionally, a QC standard prepared from high purity metals or salts, sourced from Alfa Aesar (Heysham, UK) and Spex CertiPrep (Stanmore, UK), was prepared in 6% nitric acid at levels that matched the CRMs.

Table 1 Certified Concentrations of the CRMs ($\mu\text{g/g} \pm$ expanded uncertainty, $k=2$)

	Cr	Cd	Hg	Pb
BCR 680	114.6 ± 2.6	140.8 ± 2.5	25.3 ± 1.0	107.6 ± 2.8
ERM EC681k	100 ± 5	137 ± 4	23.7 ± 0.8	98 ± 6

Sample Preparation

Microwave digestion was employed (Multiwave 3000, Anton Paar Ltd, UK) to ensure complete dissolution of the interlaboratory comparison sample (polypropylene) and CRMs. Approximately, 0.1 g of the plastic material was weighed into a quartz weighing boat and the boat was inserted into the quartz digestion vessel. Then 6 ml of concentrated nitric acid and 2 ml hydrogen peroxide (SuperPurity, Romil, UK) were added. The microwave program used is detailed in Table 2. A

digested calibration standard and blank were included in each batch. After digestion, the samples were made up to 100 g with high purity water (18 MΩ cm, Elga-Maxima, UK). For IDMS, after weighing the sample, an appropriate amount of isotopically enriched spike was added to the boat (0.50 g for the interlaboratory comparison sample, 0.35 g for CRM) to give a gravimetric ratio of 1, before inserting into the microwave vessel and continuing as above.

Table 2 The Multiwave 3000 Microwave Conditions

Stage	Power (W)	Ramp (min)	Hold (min)
1	600	5	15
2	1400	10	10
Allow to cool to room temperature			
3	1400	15	30
4	0	10	10

Instrumentation

An Agilent 7500ce ICP-MS instrument equipped with an Octopole Reaction System (ORS) and Integrated Sample Introduction System (ISIS) was used in this study. The Integrated Sample Introduction System (ISIS) was used in high sample throughput mode with constant flow nebulization set at 0.1 rps during the analysis and washout in order to minimize overloading of the sample introduction system and the plasma with matrix components. The effect of $^{40}\text{Ar}^{12}\text{C}$ on ^{52}Cr , $^{37}\text{Cl}^{16}\text{O}$ on ^{53}Cr , and $^{95}\text{Mo}^{16}\text{O}/^{97}\text{Mo}^{16}\text{O}/^{98}\text{Mo}^{16}\text{O}$ on $^{111}\text{Cd}/^{113}\text{Cd}/^{114}\text{Cd}$ respectively were checked to ensure removal and correction of interferences. In the case of Mo, neither the samples nor CRMs contained any detectable levels, therefore mathematical correction or the use of collision gas was not necessary for the determination of Cd. As a result, Cr was measured in helium mode and Cd, Hg and Pb were monitored in standard mode. Additionally, gold was added to the rinse solution (approximately 5 µg/g) and to the internal standard used for external calibration. The use of gold shortens Hg washout time considerably, reducing the possibility of carryover. The typical instrumental operating conditions are given in Table 3.

Table 3 Typical ICP-MS Operating Conditions

Parameter	Cr, Cd, Hg, Pb	
RF Power (W)	1520	
Carrier gas (l/min)	0.88	
Makeup gas (l/min)	0.27	
Nebulizer	Glass concentric, MicroMist®	
Spray chamber	Quartz, Scott Double Pass, cooled to 2 °C	
Cones	Ni	
Parameter	Cr	Cd, Hg and Pb
Cell gas	He	None
Cell gas flow rate (ml/min)	4.0	-
Extract 1 (V)	2.1	2.1
KED	3	3
External Calibration		
Parameter	Cr	Cd, Hg, Pb
Isotopes monitored	^{52}Cr , ^{53}Cr , ^{73}Ge	^{95}Mo , ^{97}Mo , ^{98}Mo , ^{103}Rh , ^{111}Cd , ^{113}Cd , ^{114}Cd , ^{195}Pt , ^{199}Hg , ^{200}Hg , ^{201}Hg , ^{202}Hg , ^{206}Pb , ^{207}Pb , ^{208}Pb
Points per peak	3	3
Integration time/mass (s)	1.5	0.3 (Hg 0.6)
Repetitions	4	4
Total acquisition time (s)	100	100
IDMS		
Parameter	Cr	Cd, Hg, Pb
Isotopes monitored	^{52}Cr , ^{53}Cr	^{98}Mo , ^{111}Cd , ^{113}Cd , ^{114}Cd , ^{199}Hg , ^{200}Hg , ^{202}Hg , ^{206}Pb , ^{207}Pb , ^{208}Pb
Points per peak	3	3
Integration time/mass (s)	0.3	0.3
Repetitions	10	10
Total acquisition time (s)	402	402

For external calibration, after measuring the calibration standards, every eight samples were bracketed by “blank, middle calibration standard, blank” to monitor signal drift. Additionally, the calibration was repeated at the end of sample analysis.

For IDMS, each sample blend was bracketed before and after with a calibration blend in the following way; reagent blanks, calibration blend, sample 1, calibration blend, sample 2, and so forth.

Data Treatment

For external calibration, ^{52}Cr and ^{114}Cd were used for quantification whereas the isotopes were summed for both Hg and Pb. In the case of Hg, this was to improve the counting statistics due to the low ionization efficiency of this element (Equation 1). For Pb, this approach helps minimize any errors caused by variations in the natural isotopic pattern which is often observed (Equation 2).

Equation 1

$$^{202}\text{Hg} = 1 \times ^{199}\text{Hg} + 1 \times ^{200}\text{Hg} + 1 \times ^{201}\text{Hg} + 1 \times ^{202}\text{Hg}$$

Equation 2

$$^{208}\text{Pb} = 1 \times ^{206}\text{Pb} + 1 \times ^{207}\text{Pb} + 1 \times ^{208}\text{Pb}$$

Internal standard corrected calibrations at the beginning and end of the sequence were averaged. Regression coefficients of > 0.999 were obtained for all the elements.

Method Validation by IDMS

The IDMS method involves the use of an isotopically enriched standard (spike) which is added to the sample in known quantities. Typically, this is measured against the most abundant natural isotope and the spike is added in order to give a ratio of the natural isotope to the spiked isotope of 1. The concentration in the material is calculated using a calibration standard prepared in the same way as the sample. This technique is called exact matching double IDMS and LGC has developed its own protocol [4]. It has been successfully applied to a variety of elements and matrices, such as lead in wine [5], selenium in yeast supplements [6] and iodine in food products [7].

For IDMS analysis, the primary NIST standards described above were combined into one solution in 6% nitric acid to give concentrations matched to the interlaboratory comparison sample at 251.2 $\mu\text{g/g}$ Cr, 32.9 $\mu\text{g/g}$ Cd, 390.2 $\mu\text{g/g}$ Hg and 465.2 $\mu\text{g/g}$ Pb. Another mixed calibration solution was also prepared which was matched to the concentrations in the CRMs at 100.1 $\mu\text{g/g}$ Cr, 137.0 $\mu\text{g/g}$ Cd, 23.7 $\mu\text{g/g}$ Hg and 98.6 $\mu\text{g/g}$ Pb. The following enriched metals were used to prepare the spike solutions: ^{53}Cr at 95.74% enrichment (Oakridge National Laboratory, USA), ^{111}Cd at 96.5% enrichment (Oakridge National Laboratory, USA), ^{199}Hg enriched to 91.95% (Oakridge National Laboratory, USA) and ^{206}Pb NIST SRM 983 at 92.1497% enrichment (NIST, Gaithersburg, USA).

The following isotope pairs were used for quantification by IDMS: $^{52}\text{Cr}/^{53}\text{Cr}$, $^{114}\text{Cd}/^{111}\text{Cd}$, $^{200}\text{Hg}/^{199}\text{Hg}$ and $^{208}\text{Pb}/^{206}\text{Pb}$. The raw intensity data was exported into Excel, corrected for either the standard or procedural blank and the concentrations were calculated using the protocol described by

Gatterick and others [4]. As mentioned previously, natural variations in Pb isotope ratios are a source of error when using IDMS; therefore natural Pb ratios were measured in the sample, CRMs and QC standard using a multicollector ICP-MS. These experimental ratio values with their associated uncertainties were used in the IDMS calculations.

Results

External Calibration

The results calculated using typical external calibration in accordance with UKAS accredited in-house procedures are shown in Table 4 with the estimated expanded uncertainties using a coverage factor of $k = 2$. This provides a level of confidence of approximately 95%. The uncertainty components include estimations of the short term precision, isotope specificity and recovery. Additionally, the instrumental limit of detection (LOD), calculated as the mean blank concentration plus three times the standard deviation ($n \geq 10$), and overall method limit of quantification (LOQ), which included all dilution factors, were determined. These values are summarized in Table 4, with quality control data, presented as % recoveries, given in Table 5.

Table 4. External Calibration Results for the Interlaboratory Comparison Plastic Sample, $n = 3$

Sample ID	Cr	Cd	Hg	Pb
External calibration ($\mu\text{g/g}$)	252.3	36.6	399.7	469.5
Expanded uncertainty ($k=2$) ($\mu\text{g/g}$)	15.1	2.9	44.0	42.3
Rel. Expanded uncertainty % ($k=2$)	6	8	11	9
Instrumental LOD (ng/g)	0.06	0.01	0.10	0.02
Method LOQ ($\mu\text{g/g}$)	3.7	0.8	17.2	1.3

Table 5. External Calibration Results for the Quality Control Samples (%recovery \pm expanded uncertainty, $k = 2$)

Sample ID	Cr	Cd	Hg	Pb
BCR 680 ($n=1$)	98.8 \pm 5.9	101.3 \pm 8.1	108.2 \pm 12	99.1 \pm 8.9
ERM EC681k ($n=1$)	-	102.1 \pm 8.2	107.3 \pm 12	99.4 \pm 8.9
Independent QC Standard ($n=1$)	99.6 \pm 6.0	101.5 \pm 8.1	102.3 \pm 11	103.5 \pm 10
Standard addition on interlaboratory comparison sample ($n=2$)	100.1 \pm 6.0	99.3 \pm 7.9	107.9 \pm 12	98.0 \pm 8.8

The results for the quality control samples by external calibration show good recoveries with respect to either certified values (Table 1) or expected concentrations and are within overlapping uncertainty ranges.

Validation using IDMS

For the interlaboratory comparison, LGC submitted the average of nine results (three batches in triplicate) using IDMS analysis. These values, along with the expanded uncertainties (incorporating all factors from the entire procedure), are presented in Table 6. Typically the largest uncertainty contributions are attributed to the instrumental measurement of the calibration and sample blends. This was taken as the %RSD of the 10 replicate ratio measurements, which were obtained by utilizing the 'Custom Database' function in the ChemStation software [8]. In order to calculate the contribution from the blend-to-blend variation, the standard deviation of the mean of the nine replicate samples was taken. The average recoveries of the CRMs (BCR 680 and ERM EC681k), the independent QC standard, and the standard additions are given in Table 7.

Table 6. Mass Fraction Results (in $\mu\text{g/g}$) for the Interlaboratory Comparison Sample by IDMS

Sample ID	Cr	Cd	Hg	Pb
Mean	254.5	36.00	392.0	460.4
Mean measurement uncertainty	1.8	0.36	8.3	2.5
Blend-to-blend variation	1.5	0.10	4.3	0.6
Combined standard uncertainty	2.4	0.37	9.4	2.6
Expanded uncertainty (k=2)	4.8	0.75	18.7	5.1
Expanded uncertainty % (k=2)	1.9	2.1	4.8	1.1

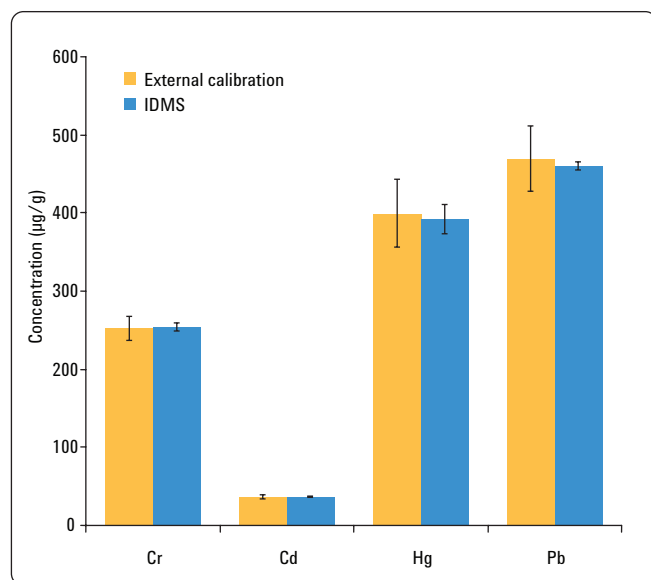


Figure 1. Comparison of external calibration and IDMS for the inter-laboratory comparison sample, with their respective expanded uncertainties (k=2).

Table 7. Average Quality Control Results (%recovery \pm expanded uncertainty, k=2)

Sample ID	Cr	Cd	Hg	Pb
BCR 680 (n=4)	98.7 \pm 3.0	100.1 \pm 1.6	103.6 \pm 6.5	96.9 \pm 2.0
ERM EC681k (n=4)	-	100.6 \pm 1.5	101.4 \pm 7.1	98.9 \pm 2.2
Independent QC Standard (n=4)	99.0 \pm 1.3	99.5 \pm 1.2	99.7 \pm 7.2	100.1 \pm 1.9
Standard addition on interlaboratory comparison sample (n = 2)	99.4 \pm 1.8	100.0 \pm 2.0	103.1 \pm 4.9	101.1 \pm 1.3

The results for the CRMs show excellent agreement with the certified values and any deviations from 100% are within the uncertainty limits for the material and measurement uncertainty. Additionally, recoveries obtained from analysis of the QC standard (in absence of matrix) using the proposed methodology, ranged between 99.0 and 100.1%. The standard addition results suggested that there is no matrix-induced bias (within the measurement uncertainty).

In order to compare the two calibration methodologies, the results for the interlaboratory comparison sample were plotted with their respective uncertainties and are presented in Figure 1. There is excellent agreement between mean values obtained using external calibration and IDMS; as expected, IDMS results showed smaller uncertainties than when using external calibration.

Furthermore, the results for the interlaboratory comparison study were collated by the organizing institute and were reported using the median and the mean absolute deviation, MADe, (where $\text{MADe} = \text{Median}(|x_i - X|) / 0.6745$, where x_i = each result; X = median of all results) due to the presence of outliers. The results are summarized in Table 8.

Table 8. Interlaboratory Comparison Study Results ($\mu\text{g/g}$)

Sample ID	Cr	Cd	Hg	Pb
LGC submitted results	254.5	36.00	392.0	460.4
Study Median	252.5	36.12	387.0	466.2
Study RSD%	12.7	3.1	5.4	5.3
n	25	24	22	18
% difference	0.8	0.3	1.3	1.3

As it can be seen in Table 8, LGC's results showed excellent agreement with the median of the study, providing validation of the IDMS method employed at the highest level. In turn, this also shows how external calibration can be used to provide accurate results for Cr, Cd, Hg and Pb in plastics.

Conclusions

This work has shown how the Agilent 7500ce ICP-MS with ORS can be used to obtain highly accurate and reproducible results by two different measurement approaches for the testing of RoHS compliance. The comparison between IDMS and external calibration showed excellent agreement for Cr, Cd, Hg and Pb in the plastic material. This demonstrates the equivalence of the two calibration methodologies while providing traceability to SI and international comparability. Additionally, it also proves that external calibration is sufficient for the purpose of compliance testing laboratories. Although IDMS is the method of choice for NMIs, it is an expensive and time consuming technique due to the cost of the enriched spike materials, the number of blends prepared, and the iterations performed per analyte. Furthermore, the use of the Octopole Reaction System with helium collision gas was demonstrated to remove the $^{40}\text{Ar}^{12}\text{C}$ interference on ^{52}Cr effectively, providing highly accurate results.

Acknowledgements

The work described in this note was partly funded by the UK Government National Measurement Office as part of the National Measurement System Chemical & Biological Metrology Knowledge Base Programme.

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© Agilent Technologies, Inc., 2009
Printed in the USA
December 8, 2009
5990-5059EN



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