Uncertainty Contributions to Isotope Dilution Analysis MC & Q-ICP-MS for Mercury Speciation

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Setting standards in analytical science

Introduction

The estimation of the uncertainty associated with an analytical measurement is increasingly being recognised as an essential part of the measurement process, allowing improved intercomparison of analytical results[1]. Isotope dilution analysis mass spectrometry (ID-MS) is regarded as a definitive analytical technique as the accuracy and precision obtainable are unsurpassed by alternative analytical methods[2] and allows the estimation of a measurement uncertainty which is directly related to S.I. units and therefore meets the highest metrological standards[3]. The presented uncertainty contributions to ID-MS and reverse ID-MS were calculated according to the principles described in the EURACHEM Guide[4]. Multicollector determinations were by a VG Axiom instrument with quadrupole determinations by a VG PQ3 instrument.

Isotope Dilution Procedure

ID-MS comprises the modification of the sample natural isotopic composition by the addition of an isotopically enriched spike material. After a sample/spike equilibration period a chosen isotope amount ratio is measured and the analyte concentration in the sample can be calculated using Equation 1which was also used as the model for the uncertainty estimations.

Species specific ID-MS requires that isotopically enriched analogues of the target analyte are synthesised, for this work ^{199}Hg enriched CH_3Hg^+ has been prepared by direct methylation,with methylcobalamin as the methyl group donor. It should be noted that, for organometallic species, the concentrations are calculated as the metallic component of the species. A detailed review of species specific ID-ICP-MS has been published[5].

$$C_X = \frac{C_s W_s M_x \times A_s - RB_s}{W_x M_s \times RB_x - A_x}$$

Equation 1: Where, for the ^{200}Hg:^{199}Hg isotope amount ratio system,

C_x = sample analyte concentration, C_s = spike analyte concentration, W_s = mass of spike M_x = RAM of the sample Hg, W_x = sample mass, M_s = RAM of the spike Hg, A_s = spike ^{200}Hg abundance, B_s = spike ^{199}Hg abundance, A_x = sample ^{200}Hg abundance, B_x = sample ^{199}Hg abundance, R = 200Hg:199Hg isotope amount ratio corrected for mass bias.

Calculating Isotope Amount Ratios From Chromatograms

Several data points on the apices of the peaks for each isotope of a particular specie in the chromatogram can be chosen and baseline signal subtracted. The isotope amount ratios can then be calculated using each pair of corresponding data points from the two peaks (Figure 1, Inset B) and subsequently corrected for mass bias effects. In this work an exponential law was applied.

The advantage of this approach is that the inherent precision is maintained and it is possible to obtain an estimate of precision from a single chromatogram. This approach is accurate only in the absence of both spectral skew and isotopic fractionation. Validation, for both MC & Q-ICP-MS, was by analysis of gravimetrically prepared solutions of both Hg^{2+} and CH_3Hg^+ having a range of isotopic compositions, example figures of merit are shown in Table 1.

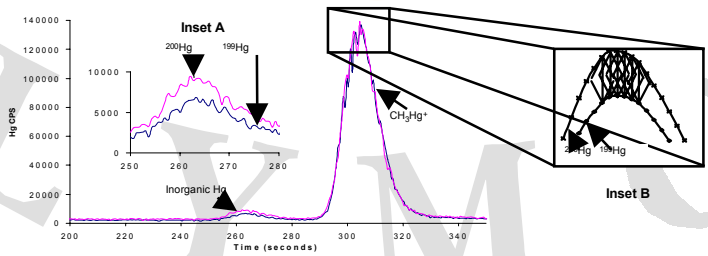

Figure 1: Separation of mercury species by HPLC with detection by Q-ICP-MS. Inset A is co-extracted inorganic Hg, ^{200}Hg:^{199}Hg isotope amount ratio of 1.37, indicating that the $CH_3{}^{199}Hg^+$ spike is stable during the equilibration process. Inset B is a schematic diagram illustrating the calculation of an isotope amount ratio from corresponding data points (arrowed) at the peak apices.

Mobile Phase: 50:50 CH_3OH:H_2O, 0.01% 2-mercaptoethanol[6]. **Flow Rate:** 0.9 ml/min

Column: Hichrom Kromasil 100-5 C18 250mm x 4.6 mm id

Internal Standard: 100 ng/g NIST 997 Thallium CRM for mass bias correction

Table 1: Figures of Merit for HPLC-ICP-MS Optimisation

	Gravimetric ^{200}Hg:^{199}Hg	Measured ^{200}Hg:^{199}Hg	
Q-ICP-MS	1.369 ± 0.023	1.371 ± 0.0064	Natural Abundance
MC-ICP-MS	0.2751± 0.000022	0.2755 ± 0.00057	Spike Abundance

$CH_3{}^{199}Hg^+$ Spike Characterisation by Reverse HPLC-IDMS

Reverse ID-MS comprises the addition of a natural standard to the isotopically enriched material. Two separate spike solutions were analysed. For HPLC-Q-ICP-MS analysis the uncertainty budget was dominated (>99%) by the uncertainty of the measured isotope amount ratios (Figure 2). The improved precision of the measured isotope amount ratios by MC-ICP-MS leads to greater contributions from other parameters in the ID-MS equation. 66% of the estimated uncertainty arises from the natural abundance data (IUPAC values) for the two mercury isotopes monitored (Figure 2). The spike mass fractions and standard uncertainties are shown in Table 2.

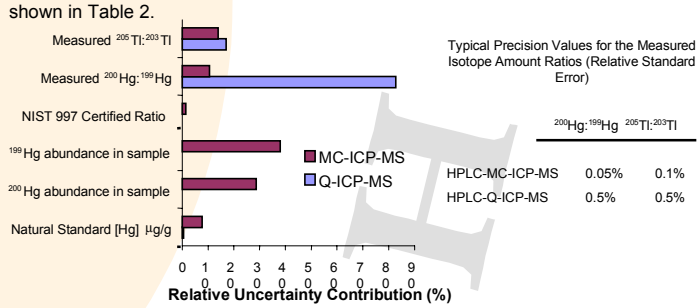

Figure 2: Uncertainty Contributions to Reverse ID-MS by MC & Q ICP-MS

Table 2: Spike Mass Fractions by Reverse IDMS

	Q-ICP-MS	MC-ICP-MS
$[CH_3{}^{199}Hg^+]$ as Hg (µg/g)	8.91	11.1
Standard Uncertainty (µg/g)	0.38	0.06
Relative Standard Uncertainty	4.3%	0.6%

Methylmercury in DORM-2 CRM by Species Specific Q-ID-MS

Each of the spike solutions characterised was used to determine the amount of CH_3Hg^+ in DORM-2 dog fish muscle CRM. The CRM was suspended in the HPLC mobile phase as the equilibration solution and an appropriate amount of spike solution added. Experiments have shown that equilibration between the particulate bound CH_3Hg^+ and the spike is complete within 400 minutes. The ^{200}Hg:^{199}Hg isotope amount ratio was determined, by HPLC-Q-ICP-MS, in samples taken after this time period had elapsed. The uncertainty contributions are shown in Figure 3 and the amount of CH_3Hg^+ determined in DORM-2 presented in Table 3.

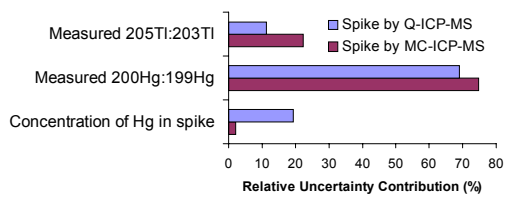

Figure 3: Uncertainty Contributions to Species Specific HPLC-Q-ID- ICP-MS

Table 3: CH_3Hg^+ in DORM-2 by Species Specific HPLC-Q-ID-ICP-MS

	Spike by Q-ICP-MS	Spike by MC-ICP-MS	Certified Value
DORM-2 $[CH_3Hg^+]$ (µg/g)	4.39	4.28	4.47
Standard Uncertainty (µg/g)	0.43	0.25	0.16
Relative Standard Uncertainty	9.7%	5.7%	3.7%

Summary

Quantitative recovery of CH_3Hg^+ from a reference material has been shown and sources of uncertainty during the measurement process have been identified for both quadrupole and multicollector HPLC-ICP-MS analysis. The use of multicollector ICP-MS improves the precision of species specific ID-MS and highlights the need to improve the isotopic characterisation of the natural abundance Hg contained within the sample.

References

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Acknowledgements: **The work described in this poster was jointly supported by LGC and the University of Plymouth.**