

Research Article

The Effect of Isotopic Composition on the Uncertainty of Routine Metal Mass Concentration Measurements in Ambient Air

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The main sources of uncertainty encountered during the analysis of the mass concentration of metals in ambient air as part of the operation of the UK Heavy Metals Monitoring Network are presented. It is observed that the uncertainty contribution from possible variation in the isotopic composition of the sample depends on the element in question, but can be significant (e.g., for Pb, Cd, and Hg). The working curve method for the ICP-MS analysis of metals in solution, with a low resolution, high throughput instrument measuring at one m/z ratio per element, relies on the relative abundance of the isotopes under consideration being the same in both the sample and the calibration solution. Calculation of the uncertainty in this analysis assumes that the isotopic composition variation within the sample and calibration solution is limited to a defined range. Therefore, in order to confirm the validity of this quantification methodology and its uncertainty budget, the isotopic composition of the calibration standards used for quantification has been determined. The results of this analysis are presented here.

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1. INTRODUCTION

The general public and the environment can be exposed to several classes of hazardous compounds containing metallic elements which occur naturally or are released by domestic or industrial processes [1]. The total concentration levels of Pb, Ni, As, and Cd allowable in the PM_{10} fraction of ambient air (particles with an aerodynamic diameter of $10\ \mu\text{m}$ or less) are now limited by European legislation [2–4]. In order to enforce this legislation, to measure human and environmental exposure, and to show compliance with limit and target values, the total concentration levels of ambient metals, at multiple sites on nationwide air quality monitoring networks, need to be measured. To this end, nationwide networks for the measurement of a wide range of particulate-borne and gaseous pollutants are now well established in many developed countries around the world. NPL currently manages and operates the UK Heavy Metals Monitoring Network (the “network”) on behalf of the UK Department for Environment, Food and Rural Affairs (Defra). The “network” consists of 24 monitoring sites around the UK

collecting PM_{10} particulate matter which is then sent back to NPL for the analysis of the mass concentration of Ni, As, Cd, Pb, (as required by European legislation) and also Hg, Cr, Cu, Fe, Mn, V, Zn, and Pt to contribute to long-term UK data sets [5]. Whilst the data quality objectives laid down by the air quality legislation are not especially exacting—the maximum allowable expanded uncertainty for Pb determination is 25%, and for Ni, As, and Cd is 40%—it is still necessary to ensure that these objectives are routinely and consistently met. Additionally NPL also sets a self-imposed maximum measurement uncertainty of 40% on the nonmandated metals.

To determine the mass concentration of particulate-phase metals in ambient air, particles are collected onto air filters which are then digested in acid before being analysed by inductively coupled plasma-mass spectrometry (ICP-MS). The ICP-MS is calibrated by a working curve method using matrix matched solutions prepared from commercially available elemental solutions certified for metal mass fraction, and compared with NIST standard reference material (SRMs) by NPL to ensure consistency and accuracy. Whilst

NPL includes a component of uncertainty to take account of the possibility of the isotopic composition of metals in ambient air varying within natural limits, for a working curve method this assumes that the isotopic composition of the calibration standards being used also falls within this assumed range. If it does not, then an additional uncertainty contribution, or a correction factor, may need to be applied. In order to validate this hypothesis, the isotopic composition of the standards used for these routine analyses requires measurement. This work presents the results of this analysis and the effect of these findings on the uncertainty budget of the measurement. We also present the contributions to overall uncertainty budget from the possible variations in the isotopic compositions of the ambient air samples.

2. EXPERIMENTAL

Particulate samples were taken at all sites in the “network” using Partisol 2000 instruments (fitted with PM₁₀ heads) operating at a calibrated flow rate, nominally of 1 m³·h⁻¹, in accordance with European standard method EN 12341 [6]. Samples were taken for a period of one week [7] onto 47 mm diameter GN Metrical membrane filters. The analysis for particulate-phase metals took place using a PerkinElmer Elan DRC II ICP-MS, following NPL’s UKAS accredited procedure, which is fully compliant with the requirements of European standard method EN 14902 [8] (the EU “reference method” for the analysis of metals in ambient air). Upon arrival at NPL, the filters sampled with particulate matter were cut accurately in half, and each portion digested at temperatures up to 220 °C using a CEM Mars X microwave. The digestion mixtures used were as follows.

- (i) Hg and Pt: 5 ml of nitric acid and 5 ml hydrochloric acid.
- (ii) All other metals: 8 ml of nitric acid and 2 ml hydrogen peroxide.

These digested solutions were then diluted with deionised water (Millipore, Milli Q, Mass, USA) prior to analysis. ICP-MS analysis took place as previously described [9] using at least four-matrix-matched gravimetrically prepared calibration solutions [10] prepared from monoelemental standard solutions (VWR, checked for total elemental composition against the NIST SRM 3100 series). A detector dead time correction was applied [11] and a full span dual detector linearity check was performed in order to minimise any detector nonlinearity [9] since the concentration of different isotopes within the samples may span several orders of magnitude. A quality control standard was repeatedly analysed (after every two solutions), and the change in response of the quality control standard was mathematically modelled to correct for the long-term drift of the instrument. The short-term drift of the ICP-MS was corrected by the use of an internal standards mixture (containing Y, In, Bi, Sc, Ga, and Rh) continuously added to the all samples via a mixing block. Each sample was analysed in triplicate, each analysis consisting of five replicates. For each element, one isotope at one m/z value was

chosen and monitored. The mass of each metal in solution (and its uncertainty) was then determined by a method of generalised least squares using XLGENLINE (an NPL-developed programme [12]) to construct a calibration curve. The analysis of the isotopic ratios of the calibration standards was performed by determining the blank-corrected intensity at each appropriate m/z ratio. The isotopic composition of the calibration standards was measured by analysing the separate monoelemental standard solutions used to make up the calibration solutions. All the usual corrections for isobaric and polyatomic corrections were applied. The mass fraction of the sum of all isotopes of metal analyte in each standard solution was approximately 1 µg/g. All isotopes of the elements of interest were measured, not simply the ones used for quantification. Whilst no additional effort was made to determine additional corrections for isotopes not usually used for quantification by the NPL procedure, additional type-B uncertainty components were included in the uncertainty budget to account for unresolved inaccuracies owing to mass bias and mass discrimination effects, based on conservative estimates from existing literature data [13]. Given the low precision of the measurements, these factors are expected to have a minimal contribution to the overall uncertainty [14]. Uncertainty contributions were also added to account for residual dead time effects and detector nonlinearity. Matrix effects were minimised by the matrix matching of all solutions prior to analysis. Total expanded measurement uncertainties for each analysis are calculated using a full GUM [15] approach and are expressed with a coverage factor of $k = 2$ representing the 95% confidence interval.

3. RESULTS AND DISCUSSION

The working curve method for the ICP-MS analysis of metals in solution, with a low resolution, high throughput instrument measuring at one m/z ratio per element relies on the relative abundance of the isotopes under consideration being the same in both the sample and the calibration solution. If this is not the case, a multiplicative bias in the observed results for element X , δ_X , will be observed, and is given by

$$\delta_X = \frac{n_{a,\text{cal}} \cdot \sum_i n_{i,\text{sam}}}{n_{a,\text{sam}} \cdot \sum_i n_{i,\text{cal}}}, \quad (1)$$

where $n_{a,\text{cal}}$ is the amount of isotope a of element X in the calibration standard, $\sum_i n_{i,\text{cal}}$ is the amount of all isotopes of element X in the calibration standard, $n_{a,\text{sam}}$ is the amount of isotope a of element X in the sample, and $\sum_i n_{i,\text{sam}}$ is the amount of all isotopes of element X in the sample [16]. When the relative abundance of the isotope used for quantification in both the sample and the calibration solution is the same, then $\delta_X = 1$ and no bias is observed. It is interesting to note that the isotopic composition with respect to the other isotopes not used for quantification has no effect on the measurement. (As and Mn are also measured by the “network,” but are monoisotopic and therefore not considered as part of this treatment).

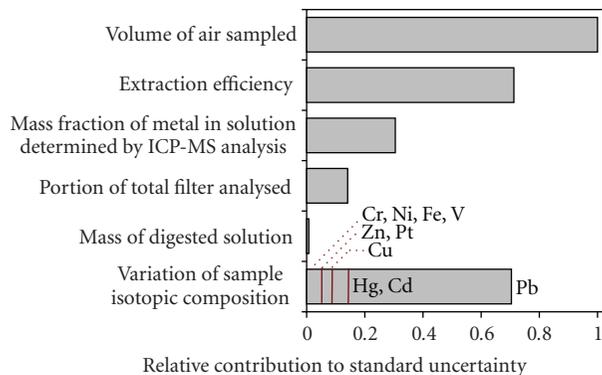


FIGURE 1: Relative contributions to the standard uncertainty of the determination of metal mass concentration in ambient air, as part of the UK Heavy Metals Monitoring Network. This example shows a measurement with an overall expanded uncertainty at the 95% confidence interval of approximately 20%. The changing uncertainty contribution from the variation in the sample isotopic composition for the different metals measured by the “network” is indicated by the additional lines and labelling on the bottom bar.

Rather than assess the isotopic composition of each individual sample, the uncertainty budget developed for this measurement includes a component of uncertainty to recognise that the isotopic composition of the sample may fall anywhere within the range of natural variations, or the representative isotopic composition, whichever is the larger range [17]. (The actual range of isotopic composition in environmental samples may be considerably narrower [18].) In practice, this assumption assigns $\delta_X = 1$ but imposes a relative uncertainty on this value equal to the possible range of isotope abundances expected for the isotopes used for quantification. Relatively little detail exists in the literature on the isotopic composition of metals in ambient air particulates. The vast majority of the work that has been published has been on Pb isotopic composition, where the greatest variation is expected. Determination of isotope ratios has been mostly used as a route to determining the origin of the Pb sampled, particularly with regard to specific industrial processes or long-range pollutant transport [14]. One study [19] has examined the Pb isotopic composition in deposition in order to compare how this changed before and after the closure of a local Pb mine. Others studies [20, 21] have used the changing Pb isotope ratios in ambient particulate matter to demonstrate the seasonal variation long-range transport of pollutants across the Asian continent. Measured Pb isotope ratios have also been used as a route to determine the changing origins of Pb emissions in an urban environment during and after the phasing out of leaded petrol [22]. Cu and Zn isotope ratios have been analysed near a large Zn refinery [23] as a means of determining the origin of metallic ores, and Sr and Nd isotope ratios have been used in the discrimination of emissions from various industrial sources and traffic emissions, respectively [24]. In all cases, the observed ranges of the isotopic compositions fell well within the natural ranges predicted [17] and these natural ranges have been used to construct the uncertainty

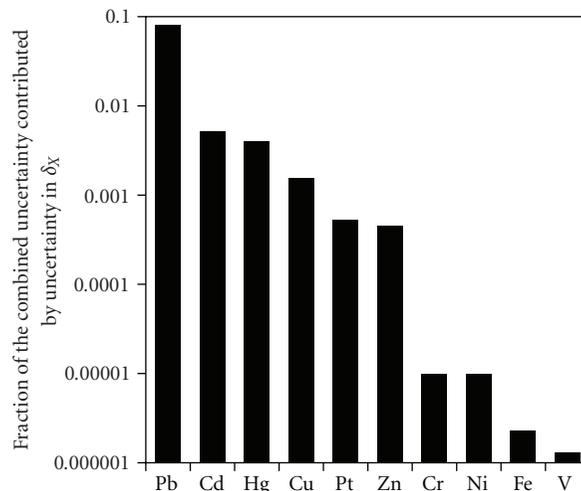


FIGURE 2: The fraction of the overall measurement uncertainty for each metal contributed by the uncertainty in δ_X .

budget presented in this paper. Moreover, when the isotopic composition of samples under consideration in this study has been measured periodically, the abundance of the isotope used for quantitation has always been well within these ranges as well [25]. The major contributions to the overall measurement uncertainty for the determination of the mass concentration of metal in ambient air are shown in Figure 1.

As can be seen, the contribution from the possible variation in the isotopic composition of the sample is strongly dependent on the element being determined. This contribution is very significant for Pb, significant for Hg, and Cd, less significant for Cu, Zn and Pt, and negligible for Cr, Ni, Fe, and V. This is highlighted in Figure 2 which shows the fraction of the overall measurement uncertainty contributed by uncertainty in the isotopic composition of the sample being measured [25]. As expected from the data in Figure 1, this contribution is very significant for Pb, notable for Hg, Cd and possibly Cu, and insignificant for all other elements.

The summary uncertainty budget presented in Figures 1 and 2 (and the measurement equation from which this has been developed) is only valid if the abundance of the isotope used for quantification in the calibration standards also falls within this range allowed for the samples. If it does not, then an additional uncertainty contribution, or a correction factor, may need to be applied. This is not something that may be taken for granted since the calibration standards may often have been prepared from isotopically enriched pure materials, and must be measured in order to determine whether an increase in the uncertainty estimate for the overall determination was required. The results of the determination of the isotopic composition of the calibration standards used are shown in Figures 3(a) and 3(b) which show that the majority of isotopes demonstrated good agreement between the measured value and the expected range of isotopic abundances. Table 1 highlights the level of this agreement for the isotopes used for quantification.

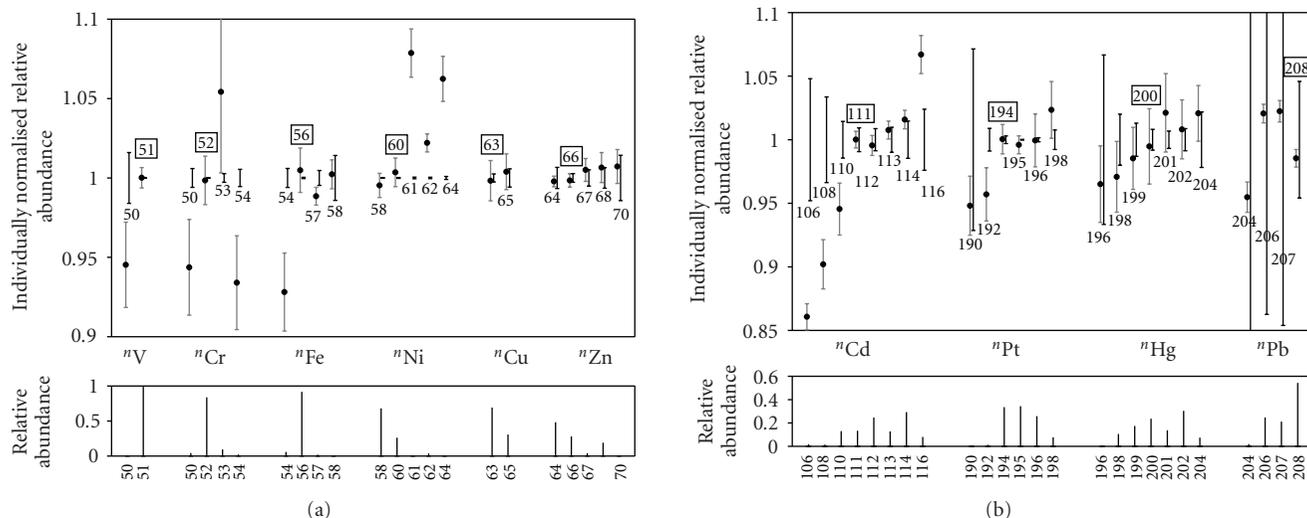


FIGURE 3: (a) V, Cr, Fe, Ni, Cu, and Zn: comparison of the measured relative isotopic abundance of the calibration standards (black circles, with the grey bars representing the standard error of the mean) against the expected range in natural, or representative, isotopic compositions (whichever is the larger range) (black bars). The relative atomic mass number is displayed for each isotope, with the boxed number being the isotope used for the quantification of the samples. Values are normalised to the centre of the natural (or representative) composition range for each isotope. The relative abundance is displayed for each element in the separate plot beneath the main chart. (b) Cd, Pt, Hg, and Pb: comparison of the measured relative isotopic abundance of the calibration standards (black circles, with the grey bars representing the standard error of the mean) against the expected range in natural, or representative, isotopic compositions (whichever is the larger range) (black bars). The relative atomic mass number is displayed for each isotope, with the boxed number being the isotope used for the quantification of the samples. Values are normalised to the centre of the natural (or representative) composition range for each isotope. The relative abundance is displayed for each element in the separate plot beneath the main chart.

TABLE 1: Agreement between the measured abundances for the isotopes used for quantifications and the expected abundance ranges.

Isotope used for quantification	Agreement with predicted range
^{50}V	No, +0.01%
^{52}Cr	No, -0.1%
^{56}Fe	No, +0.4%
^{60}Ni	No, +0.3%
^{63}Cu	Yes
^{66}Zn	Yes
^{111}Cd	Yes
^{194}Pt	Yes
^{200}Hg	Yes
^{208}Pb	Yes

Where there is agreement with the predicted range, we may assume that the uncertainty budget for the measurement already covers the expected range of isotopic compositions for both sample and calibration standard. Where Table 1 shows a lack of agreement, an additional component of uncertainty equal to the discrepancy in agreement needs to be added to justify the uncertainty statement. Given the large overall measurement uncertainties reported for the measurement of metal mass concentration in ambient air, these small additional uncertainty components are unlikely to increase the overall uncertainty of the measurement significantly. (An additional component of uncertainty has

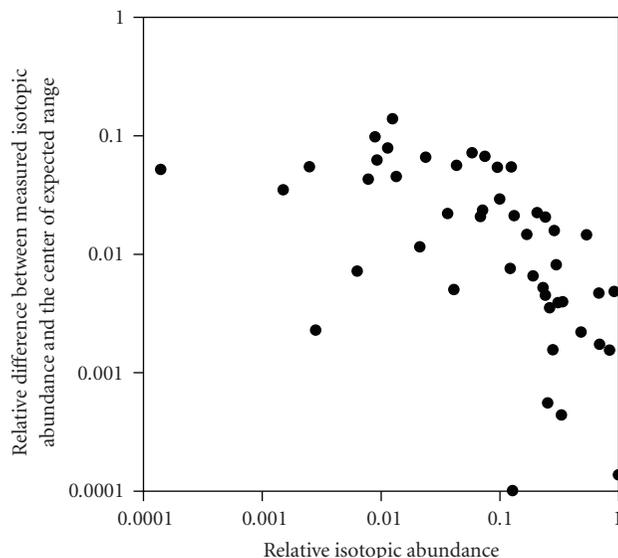


FIGURE 4: The relationship between the relative isotopic abundance of all the isotopes considered and the relative difference between the measured isotopic abundance and the centre of the expected range of isotopic abundance.

been added, rather than adding a term into the uncertainty budget to correct for bias, since in all cases the standard error of the mean of the isotopic composition measurements is greater than the observed disagreement in all cases, and

thus a bias correction term is not justified.) Perhaps not surprisingly, Table 1 highlights that a disagreement was found for the elements with the smallest predicted range of isotopic compositions, where the accuracy of the isotopic measurement is more critical.

A brief inspection of Figures 3(a) and 3(b) suggests that the bias between the measured isotopic abundance and the centre of the expected range of isotopic abundances shows some tendency to increase as the isotopic abundance decreases. This relationship is plotted in Figure 4. Since the isotopes used for quantification are generally ones with high abundances, little attention is usually paid to the less abundant isotopes, and therefore, there may well be more bias in these measurements owing to unresolved interferences, unresolved detector nonlinearity, and instrument instabilities which have a larger proportional effect on the measurement results than for high abundance species.

4. CONCLUSIONS

A summary of the main sources of uncertainty encountered during the analysis of the mass concentration of metals in ambient air as part of the operation of the UK Heavy Metals Monitoring Network has been presented. It has been observed that the uncertainty contribution from possible variations in the isotopic composition of the sample depends on the element in question, but can be significant (as in the cases of Pb, Cd, and Hg). The working curve method for the ICP-MS analysis of metals in solution, with a low resolution, high throughput instrument measuring at one m/z ratio per element relies on the relative abundance of the isotopes under consideration being the same in both the sample and the calibration solution. Calculation of the uncertainty in this analysis assumes that the isotopic composition variation within the sample and calibration solution is limited to a defined range.

The results of the isotopic analysis of these calibration standards have shown that the isotopic composition of the calibration standards agrees with the expected range of isotopic comparisons in the samples for all but four elements. In these cases, additional uncertainty components were required to be added to the uncertainty budget to account for this bias, although the increase in the overall uncertainty of the measurement was not significant. It is interesting to note that the isotopic composition with respect to the other isotopes not under consideration not used for quantification has no effect, in theory, on the measurement.

The bias between the measured isotopic abundance and the centre of the expected range of isotopic abundances shows some tendency to increase as the isotopic abundance decreases. It has been suggested that since the isotopes used for quantification are generally ones with high abundance and little attention is paid to the lower abundance isotopes, the bias in these measurements may well be due to unresolved interferences, unresolved detector nonlinearity, and instrument instability which have a larger proportional effect on the measurement results than for high abundance species.

In future, it may be expeditious to determine more rigorously the isotopic composition of samples collected

across the “network” so that the uncertainty contribution from δ_X for the elements where this is most significant (in particular Pb) may be reduced, thereby reducing the overall measurement uncertainty.

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