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Observation of a physical matrix effect during cold vapour generation measurement of mercury in emissions samples

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HIGHLIGHTS

- A matrix effect for CV-AFS measurement of mercury in emissions samples is reported.
- This results from the different efficiencies of liberation of reduced mercury.
- There is a good correlation between solution density and the size of the effect.
- Several methods to overcome the bias are presented and discussed.

GRAPHICAL ABSTRACT

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ABSTRACT

The observation of a physical matrix effect during the cold vapour generation–atomic fluorescence measurement of mercury in emissions samples is reported. The effect is as a result of the different efficiencies of liberation of reduced mercury from solution as the matrix of the solution under test varies. The result of this is that peak area to peak height ratios decease as matrix concentration increases, passing through a minimum, before the ratio then increases as matrix concentration further increases. In the test matrices examined – acidified potassium dichromate and sodium chloride solutions – the possible biases caused by differences between the calibration standard matrix and the test sample matrix were as large as 2.8% (relative) representing peak area to peak height ratios for calibration standards and matrix samples of 45 and 43.75, respectively. For the system considered there is a good correlation between the density of the matrix and point of optimum liberation of dissolved mercury for both matrix types. Several methods employing matrix matching and mathematical correction to overcome the bias are presented and their relative merits discussed; the most promising being the use of peak area, rather than peak height, for quantification.

1. Introduction

Mercury's toxicity and ability to bio-accumulate make it one of the most important global environmental pollutants currently. As a direct result its emissions to, and presence in, aquatic and terrestrial biosystems are regulated and assessed by national and international legislation (as an example, the recently signed UNEP Minimata Convention on Mercury) [1]. A measurement infrastructure providing traceability and accurate measurement methods is essential in supporting this legislation, not least for direct emissions of mercury from stationary sources [2].

Measurements of mercury collected in impingers from stationary source emissions according to EN 13211 [3] and EN 1483 [4] are performed using reduction of the mercury species present to

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elemental mercury by stannous chloride, desorption via an argon gas flow bubbling through the impinger solution, and measurement using cold vapour atomic fluorescence spectroscopy. This is the analytical method of choice because it is generally considered to be insensitive to the sample matrix since the mercury in the sample is separated from the matrix for analysis. Furthermore, since the matrix is not analysed it is an improvement over techniques such as ICP-MS, which do additionally analyse the matrix and struggle to cope with the very high ionic content of such test samples [5]. Because the measurement regime is kept constant it is generally assumed that the fluorescence profile as a function of time is similarly constant resulting in a constant ratio between peak height (h) and peak area (A) – this is certainly the case for the analysis of gaseous phase mercury collected on solid phase mercury adsorption tubes using previously published methods [6,7] – see Fig. 1. This shows that the relationship between peak height and peak area is consistent and shows relatively low variance until peaks heights below 10 (approximating to mercury masses below 100 pg) are reached. Below this level the relationship is less precise and shows some evidence of positive bias in favour of peak area because of the difficulty of automatically assigning baselines when integrating these small peak areas.

For these above reasons peak height is usually used for quantification because it may be determined with greater precision (not needing an accurate assessment of baseline as for peak area) and is also much more accurate at very low concentrations (where baseline allocation difficulties may produce significantly biased, or negative, peak areas). This generally works well for the measurement of gaseous mercury on absorption tubes and this assumption in most usually transferred to reduction and desorption measurement of mercury in solution because of the assumed matrix insensitivity of the method. However, we report for the first time a physical matrix effect associated with the measurement of mercury in liquid test samples using the reduction and desorption methods which may impose measurement biases of up to 2.5% if peak height is used for quantification. This physical matrix effect results from differences in the efficiency of removal of the reduced mercury between test samples and calibration solutions as a result of a mismatch of physical properties between these two types of solution. This demonstrates that under these conditions the reduction and desorption technique is not completely matrix insensitive. Whilst some papers have examined emissions inventories and source apportionment for mercury [8–10] employing well know standard methods [11,12], little work exists to investigate the measurement science of the laboratory based analytical techniques or develop these further. Recent work has investigated optimum strategies for the calibration of automated measurements of mercury in impinger solutions collected from stationary sources [13].

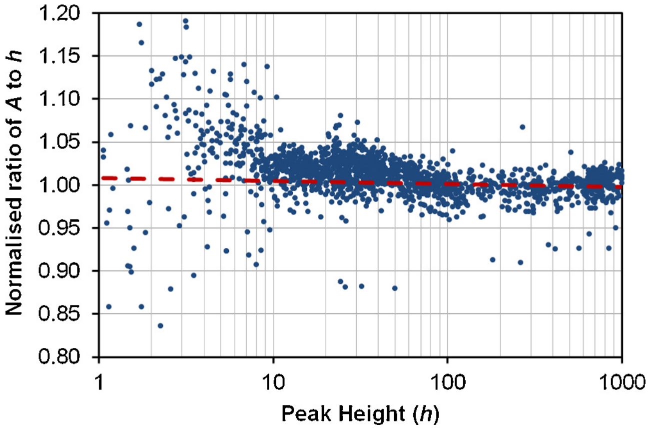

Fig. 1. The normalised peak area (A) to peak height (h) ratio as a function of h for 1850 determinations of the mass of Hg trapped from ambient air onto gold coated silica adsorption tubes over 10 years at NPL. Whilst the absolute mass depends on the temporal variation of instrumental parameters the masses of mercury measured range from approximately 10 ng (at $h = 1000$) to 10 pg (at $h = 1$). The red dashed line represents the least squares best fit to the data. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2. Experimental

2.1. General

All experimentation was conducted in an air conditioned laboratory (20 ± 2 °C). Ultra-pure analytical grade reagents were used throughout (Fisher, UK) and solutions were made up gravimetrically in thoroughly cleaned polypropylene-ware with deionised water (18.2 MΩ cm, Purelab Flex 2, Elga).

2.2. Solution preparation

Real test samples (collected from a waste incineration plant in the south of the UK) and synthetic analogues have been analysed containing mercury at mass concentrations of between 1 and 0.1 ng mL^{-1} dissolved in dichromate impinger solutions (0.05 g g^{-1} $K_2Cr_2O_7$ in 0.2 g g^{-1} HNO_3) (as would obtained from sampling according to EN 13211), subsequently diluted to various extents with 0.02 g g^{-1} HCl. (In fact, because the ratio of peak area to peak height is being examined, which, for a given matrix, is independent of the actual mercury concentration (providing we are operating away from the detection limit) the absolute accuracy of solution concentrations is not crucial.) The sodium chloride solutions also measured in this study were prepared gravimetrically from high purity NaCl (Fisher, UK) in a 0.02 g g^{-1} HCl matrix containing mercury at mass concentrations of between 1 and 0.1 ng mL^{-1}.

2.3. Analysis by cold vapour atomic fluorescence spectroscopy

The analysis was performed using NPL's ISO 17025 accredited in-house method based on the requirements on EN 13211 and in turn those of EN 1483 [4], using reductive desorption with $SnCl_2$ (0.02 g g^{-1} $SnCl_2$ in a 0.1 g g^{-1} HCl) and a stream of argon (99.999%, BOC) bubbled through the solution and then measurement with cold vapour atomic fluorescence spectroscopy (PS Analytical, Millennium Merlin).

Samples were prepared for the CV-AFS in polypropylene centrifuge sample tubes (50 mL, Fisher) and loaded into an autosampler (PSA 20.400 Autosampler). During analysis the sample is taken into the CV-AFS via peristaltic pumps along with the reagent blank (0.02 g g^{-1} HCl) and reductant (0.02 g g^{-1} $SnCl_2$ in 0.1 g g^{-1} HCl) where they are combined in a reaction chamber. The 'mid' sensitivity range was used throughout. Samples were introduced using an autosampler (PSA 20.400) using '100%' pump speed. All mercury present is reduced to elemental mercury by the stannous chloride. The solution then enters the gas–liquid separator (GLS) where a high purity stream of argon is injected. The argon bubbling through the GLS assists desorption of the elemental mercury into the vapour phase. The gaseous elemental mercury produced is passed through a dryer tube ('PermaPure' system) where any moisture is removed prior to entering the fluorescence detector. Once in the detector the elemental mercury absorbs radiation from a mercury lamp at 253.7 nm and subsequently re-emits this as fluorescence, also at 253.7 nm, with an intensity proportional intensity to the amount of mercury present. All measurements were blank corrected, although the blank levels observed were always much less than 1% (relative) of