

International System of Units Traceable Results of Hg Mass Concentration at Saturation in Air from a Newly Developed Measurement Procedure

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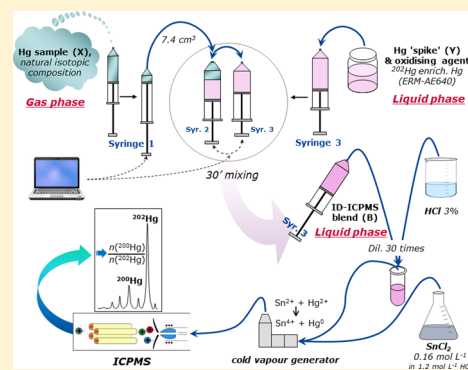
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S Supporting Information

ABSTRACT: Data most commonly used at present to calibrate measurements of mercury vapor concentrations in air come from a relationship known as the “Dumarey equation”. It uses a fitting relationship to experimental results obtained nearly 30 years ago. The way these results relate to the international system of units (SI) is not known. This has caused difficulties for the specification and enforcement of limit values for mercury concentrations in air and in emissions to air as part of national or international legislation. Furthermore, there is a significant discrepancy (around 7% at room temperature) between the Dumarey data and data calculated from results of mercury vapor pressure measurements in the presence of only liquid mercury. As an attempt to solve some of these problems, a new measurement procedure is described for SI traceable results of gaseous Hg concentrations at saturation in milliliter samples of air. The aim was to propose a scheme as immune as possible to analytical biases. It was based on isotope dilution (ID) in the liquid phase with the ²⁰²Hg enriched certified reference material ERM-AE640 and measurements of the mercury isotope ratios in ID blends, subsequent to a cold vapor generation step, by inductively coupled plasma mass spectrometry. The process developed involved a combination of interconnected valves and syringes operated by computer controlled pumps and ensured continuity under closed circuit conditions from the air sampling stage onward. Quantitative trapping of the gaseous mercury in the liquid phase was achieved with 11.5 μ M KMnO₄ in 2% HNO₃. Mass concentrations at saturation found from five measurements under room temperature conditions were significantly higher (5.8% on average) than data calculated from the Dumarey equation, but in agreement (−1.2% lower on average) with data based on mercury vapor pressure measurement results. Relative expanded combined uncertainties were estimated following a model based approach. They ranged from 2.2% to 2.8% ($k = 2$). The volume of air samples was traceable to the kilogram via weighing of water for the calibration of the sampling syringe. Procedural blanks represented on average less than 0.1% of the mass of Hg present in 7.4 cm³ of air, and correcting for these blanks was not an important source of uncertainty.



One of the objectives of European Union Directives 2008/50/EC and 2004/107/EC is to “ensure that adequate information on concentrations of [...] mercury [...] in ambient air [...] is obtained”. The European legislation, however, does not provide target values for mercury in ambient air. This is in part because there is not yet agreement on a procedure allowing SI (international system of units) traceable and sufficiently accurate calibrations of the mercury vapor measurement equipment. The European Parliament Directive 2010/75/EU on Industrial Emissions does specify a limit value of 50 μ g/m³ for plants bound by this legislation, but similar issues with the

lack of SI traceability exist for measurements made under this Directive. Analogous regulations are found in other countries, with similar limitations regarding quantitative measurements of Hg concentrations in air samples. For instance, in the United States of America (USA), in 2005 the Clean Air Mercury Rule was introduced to limit mercury emissions from power stations, but this legislation was abandoned in 2008 when it became

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clear that the SI traceability required to enforce the regulation in law was absent.

Commonly, calibration is a process involving a comparison with tabulated values for the expected mass of mercury at saturation in a given volume of air at a given temperature. Several empirical equations have been proposed for the estimation of these tabulated values but results obtained may differ by 5% or more.¹ The equation most commonly used at present and historically was established nearly 30 years ago by Dumarey et al.,^{2–4} is known as the “Dumarey equation” and corresponds to the least-squares best fit of results obtained for measurements of the mercury mass concentration in air at saturation (γ_{Hg} in ng cm⁻³) between 288 and 298 K: eq 1.

$$\gamma_{\text{Hg}} = \frac{D}{T} \times 10^{-(A+[B/T])} \quad (1)$$

where T is the temperature of the air, in K, A is a constant equal to $-8.134\,459\,741$, B is a constant equal to $3240.871\,534$ K, and D is a constant equal to $3\,216\,522.61$ K ng mL⁻¹. All figures are considered significant⁴ although no information is available on the scatter of the experimental points to which this relationship was fitted. There has never been any uncertainty provided for these constants but, recently, Dumarey et al. estimated that the relative expanded uncertainty ($k = 2$) of data calculated with eq 1 is approximately 2%⁴ because of its agreement at this level with recent, but unpublished, work at the National Institute of Standards and Technology, USA.

As explained elsewhere,⁵ this expression “is recommended for use in standard methods, such as ISO 6978-2:2003⁶ and ASTM D6850-03,⁷ although some other standards simply include a reference to the “saturated vapour pressure of mercury” with no further guidance on calculation⁸”. An important reason for this absence of consensus is the discrepancy (around 7% at room temperature) observed between data calculated from eq 1 and values of mass concentrations in air calculated, assuming that the ideal gas law applies, from results of mercury vapor pressure measurements in the presence of only liquid mercury.⁹

In this context, the aim of this work was to revisit the protocol described by Dumarey et al.^{2–4} and propose a novel measurement procedure that was innovative and as immune as possible to risks of analytical errors. The approach is based on measurements by inductively coupled plasma mass spectrometry (ICPMS) of mercury concentrations in the vapor phase using isotope dilution (ID) in the liquid phase at relative expanded uncertainty levels better than 5% ($k = 2$). It allows continuous sample processing under closed circuit conditions, from the sampling of several milliliters of mercury-saturated air to the mixing in the liquid phase, for ID purposes, of this gaseous mercury. This is potentially less prone to biases than a sequential protocol based on ID in the gas phase, which would require a quantitative conversion to the gas phase of the calibration material and gastight conditions during the mixing sequence.

This paper describes the main aspects of the procedure development and of its validation and discusses in particular the combined uncertainties estimated for the first results obtained and the sources of traceability to SI of these results.

■ EXPERIMENTAL SECTION

Materials and Reagents. Tests on oxidation conditions to trap the collected mercury vapor were run with 125 mL gas washing bottles of Dreschel borosilicate glass with a sintered

bottle head (Scilabware, Staffordshire, U.K.). Two 100 cm³ plastic-coated borosilicate glass bottles from Duran (Mainz, Germany) were used as reactors for the generation of mercury vapor (described as bell-jar 1 and bell-jar 2). They were closed by “DG safety caps” with two or three ports with stopcocks. The three gastight glass syringes employed to sample the Hg vapor (with syringe 1) and mix it for ID purposes in a liquid phase (with syringes 2 and 3) were, respectively, a 10 mL (i.d. 1.46 cm, length 6 cm) TLL-XL SAL 1010 SaltLine syringe from Hamilton (Bonaduz, Switzerland) and two 25 mL (i.d. 2.304 cm, length 6 cm) 23663 syringes from Norgren Kloehn (Las Vegas, NV). Bell-jars 1 and 2 were connected in series to syringe 1 via a manually operated FEP 3-way T-shape valve (valve 1) from Bohlender GmbH (Gruensfeld, Germany). The connection to syringe 1 was through a PCTFE female luer 1/4 in.-28 UNF 1.5 mm bore (Hamilton). Connections between bell-jars and to valve 1 were through 0.5 mm i.d. PTFE capillary tubing and connectors from IDEX (Lake Forest, IL): 1/4 in.-28 nuts in PEEK with polypropylene ferrules on bell jars and a 1/4 in.-28 nut in Teflon with a polypropylene ferrule and a standard 1/4 in.-28 union in polypropylene on valve 1.

Reagent preparation was carried out into Teflon bottles. Collection and dilution of ID blend samples were done in glass vials with screw solid cap with a PTFE liner (Sigma-Aldrich, St. Louis, MO) and PE centrifuge tubes, respectively.

Unless otherwise stated, only high purity reagents were used for the preparation of solutions and cleaning of the labware, including 60% HNO₃ Ultrapur grade (Merck, Darmstadt, Germany), 33–36% HCl Ultrex grade (Baker, Deventer, The Netherlands), and ultrapure water from a Milli-Q Element system (Millipore, Bedford, MA). Oxidizing reagents tested were all Emsure grade from Merck, with 99% KMnO₄, 99.9% K₂Cr₂O₇, 99% K₂S₂O₈, and 99% AgNO₃. The SnCl₂·2H₂O used to produce Hg vapor prior to ICPMS measurements was Emsure grade from Merck. A 0.16 M solution was prepared by dissolution in 1.2 M HCl, and before use this mixture was purged with high-purity helium for at least 24 h in order to minimize contaminations.

The cleaning routine for all the labware was by immersion or by filling using the following successive 24 h steps: in diluted detergent, twice in 10% HNO₃ p.a. grade (Merck), in 3% HCl Ultrapur grade and in Milli-Q water. There was also flushing with Milli-Q water in between each step. Clean labware were dried on a clean bench in the ultraclean chemical laboratory (UCCL, class <10) of the IRMM.¹⁰

Generation and handling of gaseous mercury samples took place inside fume hoods for safety reasons. All other operations of sample preparation were carried out in the UCCL or at least under clean bench conditions (class 100).

Isotopic certified reference materials (iCRMs) from JRC-IRMM (Geel, Belgium) ERM-AE639 (natural) and ERM-AE640 (enriched in ²⁰²Hg) were used, respectively, to correct ICPMS measurements for mass discrimination effects (essentially) and as a “spike” for the preparation of ID blends. A droplet of liquid mercury was used as a source of mercury vapor, for which the natural isotopic composition according to IUPAC¹¹ was verified, as described further down. The isotope amount ratio targeted for the ID calculations was $n(^{200}\text{Hg})/n(^{202}\text{Hg})$. The value for this ratio in nature (IUPAC¹¹) is 0.7736 ± 0.0093 , whereas it is 0.7705 ± 0.0028 in the ERM-AE639 and 0.005499 ± 0.000034 in the ERM-AE640. The Hg mass fraction (g g⁻¹) in the ERM-AE640 is $(3.040 \pm 0.023) \times 10^{-6}$. Long-term storage of the concentrated ERM-AE640

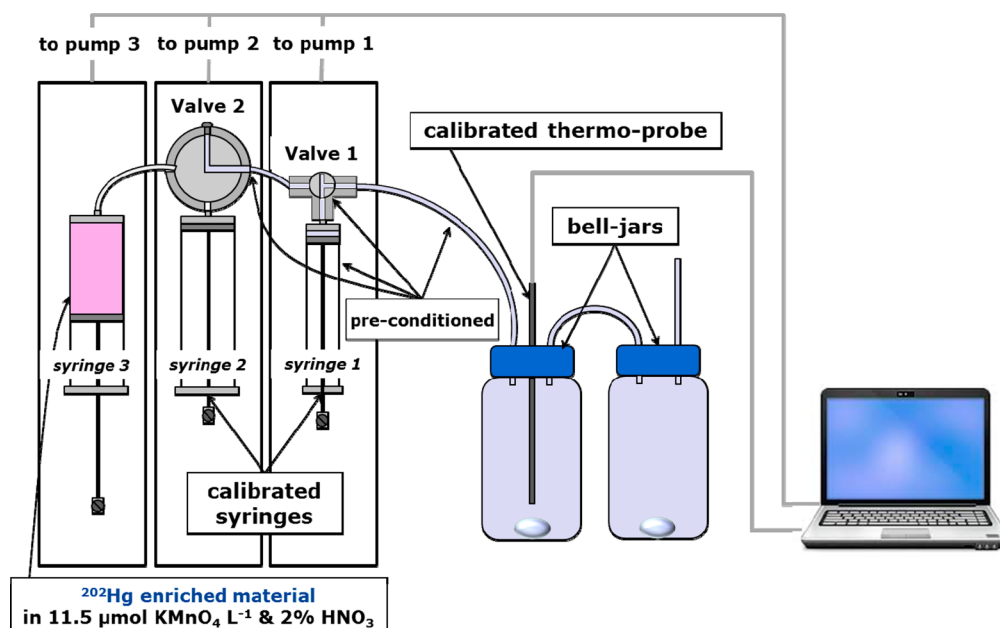


Figure 1. Experimental setup designed for this project to prepare samples: combination of interconnected valves and syringes operated by computer controlled pumps for the sampling and isotope dilution in the liquid phase of Hg vapor present in air at saturation. Valves 1 and 2 are represented in the position they have during Sequence 1 of the measurement procedure (see description in Table S-2 in the Supporting Information). These valves are rotated during the procedure to ensure sample processing under closed circuit conditions.

mother solution was done in glass vials with screw caps (and PTFE liners) from Sigma-Aldrich. Dilutions were done gravimetrically in plastic-coated borosilicate glass bottles from Duran closed with premium screw caps with PTFE-coated silicone seal, also from Duran.

Instrumentation and ICPMS Measurements. As described in Figure 1, syringes were operated via a combination of three Kloeht VersaPump 6 syringe pumps (48k resolution). A 4-way valve (valve 2) from Kloeht (38 μL dead volume) was mounted on the intermediate pump and connected to syringe 2 by screwing. Connections to valve 1 and syringe 3 were through IDEX 1/4 in.-28 nuts in PEEK. Toward valve 1 and syringe 3 there were 0.5 mm i.d. PTFE capillary tubings (15 and 12 cm length, respectively), with IDEX 1/4 in.-28 nuts Teflon connections with polypropylene ferrules. An additional 1/4 in.-28 standard union in polypropylene (IDEX) was necessary on syringe 3. Computer control of the movements of the three pumps and of valve 2 was done by programming a series of actions using Kserial, a command-driven program operating at the command line prompt.

A semiautomated process was developed to clean syringes 2 and 3 after each use with 25 mL of 2% HNO_3 ($\times 5$) and 25 mL of 3% HCl ($\times 5$), and rinsing with Milli-Q water ($\times 5$). For this purpose only syringes were, one at a time, screwed into valve 2 and mounted on pump 2 to aspirate and return (to waste), through different ports of valve 2, these cleaning solutions. Valve 2 and the capillary tubing toward syringe 3 were cleaned after each blend preparation by circulating successively, via a peristaltic pump at 18 rpm, 40 mL of 3% HCl and 20 mL of Milli-Q water for rinsing purposes.

In-situ monitoring of the temperature conditions was done online with a 1502A thermo-probe (serial number B2C247) from Fluke (Eindhoven, The Netherlands), calibrated at 0.1°C combined expanded uncertainty ($k = 2$) level (calibration certificate number 1331087) by the BELAC (the Belgian accreditation body) accredited Dimed Company in Belgium.

Weighing were carried out with a XP504 balance from Mettler-Toledo (Greifensee, Switzerland) calibrated (calibration certificate number 8665458D-K-17094-02-00) by Sartorius. Unless otherwise stated, the relative expanded uncertainty for these weighing was conservatively taken as 0.5% ($k = 2$).

ICPMS measurements were carried out with an Elan 6000 (PerkinElmer-Sciex, Ontario, Canada) equipped, for sample introduction in the liquid phase, with a pumped micro-concentric nebulizer (MicroMist, Glass Expansion, West Melbourne, Australia) and a mini-cyclonic spray chamber (Cinnabar, Glass Expansion). Sample introduction in the gas phase was done after online reduction of the mercury and using a gas-liquid separator from PerkinElmer. Mercury vapor was introduced to the ICP torch through 1 m of i.d. 0.5 mm Teflon tubing. It was pushed by argon delivered from the combination of the ordinary nebulization line (typically 0.95 L min^{-1}) and of the secondary gas line (preset to 0.16 L min^{-1}).

ICPMS Measurements. Optimization during cold vapor generation was done with a solution of ERM-AE639 at 500 pg g^{-1} . Typically, after a warm up of about 1 h, the nebulizer and secondary gas flow rates were tuned to optimize sensitivity and signal stability (see Table S-1 in the Supporting Information). The relative standard deviation (RSD) on Hg isotope ratio results under optimum conditions was typically 0.2–0.4%. ID blend solutions obtained from trapping the gaseous Hg samples were diluted 30 times with 3% HCl for ICPMS measurements, to bring the Hg mass fraction in solution also to about 500 pg g^{-1} . Counts per second signals under these conditions were approximately 46 000–56 000 and 345 000–400 000 for $m/z = 200$ and 202, respectively. The amount of Hg in procedural blanks was measured by external calibration with gravimetrically diluted solutions (in 3% HCl) of ERM-AE639. The external calibration was based on the sum of the intensities measured for isotopes ^{199}Hg , ^{200}Hg , ^{201}Hg , and ^{202}Hg , while isotopes ^{196}Hg , ^{198}Hg , and ^{204}Hg were not considered because of their low abundance.

Table 1. Equations Applied in This Project for Calculation of the Hg Mass Concentration in Air at Saturation

main equations

$$n_{X,T} = C_Y m_Y \left(\frac{R_Y - R_{B,T}}{R_{B,T} - R_X} \right) \frac{\sum (R_a)_X}{\sum (R_a)_Y} - n_{\text{blk},T} \quad (3)$$

$$\gamma_{X,T} = \frac{n_{X,T} M_{\text{Hg}}}{V_X} \quad (4)$$

intermediate level equations

$$I_{i,\text{DT_corr}} = \frac{I_i}{1 - I_i \lambda} \quad (5)$$

$$I_{i,\text{Bkg_corr}} = I_i - I_{i,\text{Bkg}} \quad (6)$$

$$r = \frac{I_{200\text{Hg,corr}}}{I_{202\text{Hg,corr}}} \quad (7)$$

$$R_B = K r_B \delta_{\text{DT}_B} \delta_{\text{Bkg}_B} \quad (8)$$

$$K_j = \left(\frac{R_{\text{AE639}}}{r_{j,\text{AE639}} \delta_{\text{DT}_K} \delta_{\text{Bkg}_K}} + \frac{R_{\text{AE639}}}{r_{j+1,\text{AE639}} \delta_{\text{DT}_K} \delta_{\text{Bkg}_K}} \right) / 2 \quad (9)$$

$$n_{\text{blk}} = \frac{\overline{m_{i,\text{blk}} I_{i,\text{blk}}}}{S_{\text{blk}} M_{\text{Hg}}} \quad (10)$$

$$V_X = \frac{m_{\text{water},\text{S1},20^\circ\text{C}}}{d_{\text{water},20^\circ\text{C}}} \quad (11)$$

parameter		index	
n	amount of substance (mol)	X	mercury-saturated air sample, natural isotopic composition taken from IUPAC, ¹¹ column 9
C	elemental amount content (mol g ⁻¹)	Y	ERM-AE640 isotopic CRM
m	mass (g)	B	isotope dilution blend between X and Y
R	$n(^{200}\text{Hg})/n(^{202}\text{Hg})$	T	temperature at sampling
(R_a)	$n(^a\text{Hg})/n(^{202}\text{Hg})$	a	Hg isotope
γ	mass concentration in air (g cm ⁻³)	blk	blank
M	molar mass (g mol ⁻¹)	i	generic index
V	volume (cm ³)	j	generic index
I	measured intensity (counts s ⁻¹)	DT	dead time effects
λ	dead time (s)	Bkg	instrumental background bias
r	measured isotope ratio	corr	correction implemented
K	correction for mass discrimination effects	AE639	ERM-AE639 isotopic CRM
δ	unity multiplicative factors carrying uncertainty associated with corrections for various effects	water	ultrapure water
S	slope of the external calibration curve for blank measurements ((counts s ⁻¹)/(g g ⁻¹))	S1	syringe 1
d	density (g cm ⁻³), taken as 0.998 ± 0.001 ($k = 1$) for ultrapure water at 20 °C		

Data Processing and Uncertainty Estimation. Signal intensities per replicate ($n = 6$) were corrected for two “additive” effects, dead-time and instrumental background, prior to calculating an average ratio and a standard error of the mean (used as standard uncertainty). Dead time was estimated according to model 2 in Nelms et al.¹² Correction for mass discrimination effects was done by external bracketing. Isotope ratios measured in the ID blends were multiplied by the average of two ratios between the certified and a measured value of the $n(^{200}\text{Hg})/n(^{202}\text{Hg})$ ratio in the ERM-AE639 solution.

Unless otherwise stated, all uncertainties were expanded uncertainties with multiplication of the standard uncertainty by a coverage factor k equal to 2 to produce an interval giving a level of confidence of approximately 95%. Combined standard uncertainties were evaluated using a mathematical model of the measurement and the law of propagation of uncertainty (partial derivatives) according to the ISO/GUM guide.¹³ In practice, a dedicated software program¹⁴ was used, based on the numerical

method of differentiation described by Kragten.¹⁵ An exception was made, however, for the propagation of the uncertainty associated with the two “additive” corrections made on signal intensities described above. Doing this through the simultaneous use of all repeatability values from all measured signal intensities could lead to an overestimation of the uncertainty on ratios. To avoid this risk and for the combined uncertainty calculations only, “additive” corrections on intensities were translated into multiplicative unity correction factors on ratios following a method described elsewhere.¹⁶

RESULTS AND DISCUSSION

Experimental Setup, Operational Conditions, and Measurement Procedure. *Main Characteristics of the Measurement Procedure Applied to Produce the Experimental Points That Led to the “Dumarey Equation”.* The measurement procedure developed to establish the “Dumarey equation” is described in Dumarey et al.^{2–4} In summary, into

the bottom of a glass vessel at atmospheric pressure, known as the bell jar, a small amount of elemental mercury was placed, such that a mercury-saturated atmosphere could develop within the vessel. A gastight microsyringe was used manually to remove mercury-saturated air via a septum in the top of the vessel, at known temperatures (recorded by a mercury thermometer inserted into the vessel). The volatile mercury in the microsyringes was transferred, manually too, by capture onto gold-coated silica absorption tubes, then thermally desorbed and measured by cold vapor atomic absorption spectrometry. The Hg mass concentration $\gamma_{\text{Hg},T}$ at saturation at a given temperature T in the volume of air $V_{\text{cal},T}$ was determined according to eq 2, by comparing the analytical response $I_{\text{cal},T}$ to I_{std} obtained from the measurement of a known mass m_{std} of mercury in a standard solution (prepared from HgCl_2 and stabilized with cysteine) using the reduction and purge method.

$$\gamma_{\text{Hg},T} = \left(\frac{m_{\text{std}}}{V_{\text{cal},T}} \right) \left(\frac{I_{\text{cal},T}}{I_{\text{std}}} \right) \quad (2)$$

Procedure validation was based on results obtained for measurements of the mercury concentration in 15 candidate CRMs. The “mean relative difference between certified and measured values across all the reference materials measured” was 0.17% and “in all but one case there was agreement between certified and measured values at the 95% confidence level”.⁴ It is however also important to note that these relative differences varied over a large range from −13% to +18%, and the mean calculated from absolute values was 5.3%. This is much higher than both the 0.17% cited above and the 2% relative expanded uncertainty ($k = 2$) proposed recently for the “Dumarey equation” data.⁴ Values estimated in 2008 by Brown et al.⁵ for ambient mercury measurements based on sampling onto a gold-coated silica adsorption tube and detection by atomic fluorescence spectrometry were also much higher. The relative expanded uncertainty ($k = 2$) was 16.7% and 13.9% if the uncertainty of sampling (inherent to the partial lack of knowledge regarding the risk of behavioral changes of the solid phase sorbent depending on whether microvolumes of concentrated Hg air samples or large volumes of diluted Hg air samples are passed through) is excluded. These budgets included a relative standard uncertainty component of 8% to account for the difference observed between calibration data obtained from measurements in air³ and those obtained from vapor correlations (with calculations of mass concentrations in air assuming the conditions of an ideal gas).⁹ When not accounting for this difference, the relative combined uncertainty ($k = 2$) on the result of a measurement of the Hg concentration in air would further reduce to 12.6% or to 8.6% if the sampling uncertainty was also excluded.

Main Characteristics of the Measurement Procedure Developed for This Project. In the current project, the objective was to develop a new procedure for SI traceable measurement results of the concentration of Hg present at saturation in the gas phase by isotope dilution in the liquid phase and measurements by ICPMS (see mathematical description in eqs 3–11 in Table 1).

The objective was also to design a system allowing the sampling of large volumes (several milliliters) of mercury saturated air, fully closed, automated, and not requesting manual interventions before the end of the air/liquid mixing sequence for ID purposes. The proposed setup consisted of two

100 cm³ glass bottles (bell-jars 1 and 2) containing 120 μL of natural liquid mercury each and connected in series to a combination of interconnected valves and syringes operated by computer controlled pumps (Figure 1). Both bell-jars remained at atmospheric pressure through a connection with a capillary tube to the outside on bell jar 1. Temperature conditions during sampling were recorded in situ via a thermo-probe inserted in bell-jar 2. Once sampled the gaseous mercury was mixed quantitatively in an oxidizing solution with the mercury from the ID “spike” material. Mercury isotope ratios in the resulting ID blends were measured by ICPMS subsequently to a cold vapor generation step (cf. illustration of the basic premise of the measurement procedure in Figure S-1 in the Supporting Information).

In each bell-jar, the mass ratio between liquid mercury and mercury vapor at saturation was greater than one million. The emission rate of gaseous mercury may change in case there is oxidation at the surface of the liquid mercury droplet (formation of mercury oxide).¹⁷ To prevent this risk, both bell-jars were shaken gently prior to each cycle of operations for gaseous mercury sampling. Moreover, it is well-known that gaseous mercury adsorbs easily on glass and plastic materials, and precautions that will be detailed below were taken to ensure permanent saturation of adsorption sites for all internal walls up until the inner body of syringe 1. Tests were also run to ensure equilibration of the mercury partial pressure from the bell-jars to syringe 1, at the time of gaseous mercury sampling.

With isotope dilution there must be full equilibration between isotopes from the sample (in this case Hg at saturation in controlled amounts of air) and from the “spike” material (in this case Hg in controlled amounts of liquid ERM-640). This condition is essential but, contrary to the more common strategy of external calibration, a quantitative recovery of the mass of the ID blend solution is not needed to proceed to the detection step by ICPMS. It is one of the essential differences with the procedure described in Dumarey et al.^{2–4}

The target $n(^{200}\text{Hg})/n(^{202}\text{Hg})$ value in the ID blend of approximately 0.12 resulted from a compromise. It took into account minimization of the theoretical ID error magnification factor¹⁸ and optimization of the signal-to-noise ratio conditions (minimization of the uncertainty arising from corrections for dead-time effects and for instrumental background) for such ICPMS isotope ratio measurements. Target values for the volume of gaseous Hg and the mass of solution containing the Hg “spike” liquid material (diluted 300 times) were obtained from iterative simulations based on theoretical ID-ICPMS calculations; 7.4 cm³ and 16 g, respectively, were eventually retained. Considerations above resulted in the use of gastight syringes of 10 cm³, 25 cm³, and 25 cm³ volumes for syringes 1, 2, and 3, respectively.

Typically, at the beginning of a cycle, syringes 2 and 1, empty, were fixed on pumps 2 and 1, respectively. Syringe 2's plunger was fully pushed up while syringe 1's plunger was left pulled to a volume of approximately 1 cm³. Bell-jar connections to syringe 1 (via valve 1) and to the atmosphere were opened. Syringe 3 enclosing the 16 g of diluted ERM-640 material was fixed on pump 3 during the sampling sequence. The measurement procedure (see details in Table S-2 in the Supporting Information) was based on the following sequences: (1) preconditioning during 100 min of all parts in connection from bell-jars to valve 2 via syringe 1, to allow the saturation of all internal surface sites with Hg atoms (sequences 1 and 2); (2) positioning of syringe 1's plunger for sampling

and re-equilibration of the partial Hg vapor pressure down to bell-jar 1 at atmospheric pressure during 180 min (sequences 3 and 4); (3) sampling of 7.4 cm³ of Hg-saturated air during 5 min, after disconnection from bell-jars and connection between syringes 1 and 2 (sequence 5); (4) mixing by exchanges between syringes 2 and 3 during 30 min, to convert the sampled gaseous Hg to an oxidized form and ensure full isotopic equilibration with the isotopically enriched Hg (sequence 6); (5) isolation, in syringe 3, and dilution of the ID blend solution, followed by a reduction of the Hg mixture to enable Hg isotope ratio measurement by ICPMS in the gas phase (sequences 7 and 8).

Development and Validation of the Measurement Procedure. This procedure was validated through an assessment of the factors influencing the results and an estimation of the uncertainty associated with these results. ISO/IEC 17025, the international standard establishing the “general requirements for the competence of testing and calibration laboratories”,¹⁹ describes these two approaches as part of a list of five that should be used, alone or in combination, for the determination of the performance of a measurement procedure. Description of the main aspects of the procedure development and discussion on its validity for this project become *defacto* inter-related.

Calibrating the Syringes and the Plungers' Movements on Pumps. Pumps were operating with stepper motors at the rate of 60 steps s⁻¹ minimum for up to 48 000 steps. Thus, numbers of steps theoretically required for moving plungers in syringes 1 and 2 (or 3) to draw in or dispense 7.4 cm³ were, respectively, 35 520 and 14 208 (from 48 000 × 7.4 divided by 10 or by 25).

Syringe calibration was done by repeated weighing of ultrapure water at room temperature. The mass of water that could be introduced in syringe 1 for a course of 35 609 steps was 7.3952 g (0.01% RSD, $n = 6$; 0.05% relative expanded uncertainty, $k = 2$). Thus, assuming conservatively a density (g cm⁻³) of 0.998 ± 0.001 ($k = 1$), this was equivalent to a volume of $7.4100 \text{ cm}^3 \pm 0.0076 \text{ cm}^3$ ($k = 1$). Transfer from syringe 1 to syringe 2 needed to be quantitative while plungers' movements needed to be synchronized to avoid the generation of pressure variations between syringes. When 35 609 steps were necessary for the course of syringe 1's plunger, the number of steps required for the course of syringe 2's plunger was 14 244 for a ratio of 2.5 between speeds (steps s⁻¹) of plungers. This ratio was however not 2.5 exactly and, after calibration from water weighing measurements, the number of steps programmed for the course of syringe 2's plunger was 14 252. The number of steps applied for syringes 2 and 3 during sequences 6 and 7 was calculated proportionally to the volumes then to be handled.

Assessing Contamination—Procedural Blanks. The measurement procedure described above was also applied to produce procedural blanks. However, instead of sampling Hg-saturated air from bell-jars via syringe 1, air from the laboratory atmosphere was aspirated directly in syringe 2 and processed (and thus syringe 1 was not used). Syringe 3 contained 16 g of 11.5 μM KMnO₄ in 2% HNO₃ (no ERM-640 of course). Thus, procedural blanks accounted for possible Hg contamination coming from ambient air, the oxidizing solution and traces of Hg left in syringes 2 and 3, valve 2, and respective connections after the cleaning procedure. Two sets of procedural blanks ($n = 3$ each) were run, and the average amounts of mercury found were $(4.9 \pm 3.4) \times 10^{-13}$ and $(3.0 + 10.0 \text{ or } -3.0) \times 10^{-13}$ mol.

Controlling the Conditions before and during the Sampling Stage. The absence of manual manipulations for

the capture of the Hg-saturated air sample was an asset in this project. It eliminated some risks of biases such as, for instance, a change of the Hg partial pressure in the sampling syringe because of the application of fingers on the syringe body and the heat that this generates. Two other potential risks of analytical errors, before and during the sampling stage, needed to be considered however. The first one was the adsorption of gaseous mercury on internal walls right before and during the transfer from syringe 1 to syringe 2 (sequence 5), thus reducing the amount of Hg effectively transferred to syringe 2. To prevent this risk, the circulation of mercury between bell-jars and syringe 1 and the interaction with internal walls was stimulated by moving back and forth the plunger of syringe 1 three times before the sampling stage, with long pauses interspersed. The second risk was a dilution of the concentration of gaseous Hg because of the air repeatedly exchanged with outside at bell-jar 1 level. The solution that was found included the use of two bell jars in series and the application of long delays between steps, with 280 min in total for sequences 1 to 4.

Tests were also conducted to ensure that the movement of the syringe 1 plunger against a syringe 1 wall saturated with adsorbed mercury did not liberate any additional mercury into the vapor phase; although it is not clear how this could be justified theoretically, because of the maintenance of saturation conditions within syringe 1 throughout. Clean air ($<10 \text{ ng m}^{-3}$ of mercury) was expelled from a syringe whose walls were saturated with adsorbed mercury. Under these conditions the contribution from desorption from the syringe walls was assessed to be less than 1 part in 10^4 of the mercury mass that would have been present in the syringe at saturation. Therefore, the effect proposed above in syringe 1, under saturation conditions, was assumed to be negligible.

Controlling the Conditions for a Quantitative Gas–Liquid Mixing. Optimization of the conditions for quantitative trapping in solution of the Hg present in the air sample, to reach isotopic equilibration with the ERM-AE640 material, included specific experiments to compare between three types of oxidizing agents at different concentration levels and to identify a proper duration for the mixing sequence.

Candidate oxidizing agents selected according to descriptions in the literature^{20–23} were KMnO₄, K₂Cr₂O₇, and K₂S₂O₈. K₂S₂O₈ was applied in combination with AgNO₃ further to recommendations found in Xu et al.²³ It is not clear why users have, most of the time, chosen to work with amounts of oxidizing agents exceeding concentrations required for Hg conversion under stoichiometric conditions by several orders of magnitude.^{20–22} For this project, such high concentration levels were not appropriate because of the risk of interference with the reducing agent during the cold vapor generation step for ICPMS measurements and the risk of contamination from the Hg present as an impurity in these reagents. The setup for these experiments consisted of reducing quantitatively approximately 92 ng of Hg present in solution and bubbling the gaseous Hg formed (via cold vapor generation) into a glass gas washing bottle under varying trapping conditions. KMnO₄ concentrations in 2% HNO₃ were tested over 4 orders of magnitude, from 0.11 to 1150 μM. Results were compared with those obtained with K₂Cr₂O₇ at 10 μM and at 1000 μM in 3% HCl, and K₂S₂O₈ at 29 μM (associated with AgNO₃ at 0.9 μM) in 3% HCl. The best result was obtained for KMnO₄ at 11.5 μM in 2% HNO₃ (with 3% reproducibility, $n = 3$) and the Hg contamination in solution at this level was not larger than 0.1

ng kg⁻¹. This was a good compromise, and the project measurements were thus run under these conditions. It was also confirmed that the excessive concentrations of oxidizing agent in solution that are often reported in the literature are not necessary for the quantitative conversion of about 100 ng of Hg.

Mixing times from 15 min to 2 h were randomly tested over 2 weeks with the syringes on their pumps. Since there was no significant difference between results, a conservative duration of 30 min was eventually chosen for the mixing stage (sequence 6 in the procedure). Experiments were also run to progressively adjust the speed of plungers and volumes to be transferred back and forth between syringes 2 and 3.

ICPMS Measurements. Commonly there are sample to sample memory effects during ICPMS measurements caused by Hg adsorption within the sample introduction system. As discussed below correcting for this problem was an important source of uncertainty. Ample rinsing was provided between every single sample (ID-ICPMS blends or ERM-AE639 solutions), for 50 min each time, in three steps and using three different solutions of 3% HCl. Following this treatment, an aliquot of the 3% HCl solution produced to prepare all dilutions was run to acquire the signal used for background corrections. This signal always corresponded to less than 0.5% of the signals from the respective ID-ICPMS blends or ERM-AE639 samples.

Uncertainty Estimation. The mathematical model used to propagate together individual uncertainty components is described in Table 1. Equations 3 and 4 were applied to calculate the Hg mass concentration at saturation in air. Equations 5–11 describe intermediate level calculations: eqs 5–7 for corrections on measured intensities and calculations of resulting isotope ratios; eqs 8 and 9 for corrections of these ratios for mass discrimination effects; and eqs 10 and 11 for blank calculations and calibration of the volume of Hg-saturated air sampled.

Relative combined uncertainties calculated for each replicate result ranged from 2.2% to 2.8% ($k = 2$). The difference originates essentially from variations in uncertainties arising from corrections applied on intensities during ICPMS measurements. As can be seen in Table 2, these sources (for the essential part the corrections for instrumental background

because of the problems of sample to sample memory effects) dominate and explain nearly one-half to two-thirds of these combined uncertainty budgets. More generally, uncertainties of experimental results are responsible for two-thirds to nearly 80% of the overall budgets. The rest is from external sources and in particular from uncertainties on the Hg isotopic composition in the air sample taken from IUPAC.¹¹

Traceability of the Results to the SI. Establishing the way in which the series of results described below are traceable to the SI is obviously a fundamental issue. Together with validation of the measurement procedure, and particularly the estimations of combined uncertainties, it contributes to bringing confidence in results. The sophistication and the level of detail with which calibrations, comparisons, and corrections that relate results to SI units must be described depend on the uncertainty targeted for this procedure. The aim is to establish that possible deficits and lack of understanding in these descriptions cannot be responsible for measurement biases and errors that would not have been corrected for while approaching or being larger than the uncertainty target. When the traceability to SI is established, results can be compared to others also traceable to SI.

Main traceability routes to SI that can be established from the equations listed in Table 1 may be described as follows. Mass values and sampled volumes V_X (via water weighing based calibration) are traceable to the kilogram. Time estimations during ICPMS measurements of signal intensities are traceable to the second via the calibration of the detector's clock (done by its manufacturer) and certified values of the iCRM used to estimate the detector's dead time value. Corrections for other signal biases (globally estimated as "mass discrimination effects") during ICPMS measurements are traceable to the certified isotope ratio values of the ERM-AE639. These isotope ratio values, those of the ERM-AE640 as well as the certified value of the Hg amount content in the ERM-AE640, are traceable to the mole and the kilogram according to routes described in the certificates of these materials. The same reasoning applies to natural isotopic abundances taken from IUPAC¹¹ and justifications provided therein. Finally, although temperature measurement results are not needed in calculations described in Table 1 they are used to enable comparisons of Hg mass concentration results with other data sets. The traceability to SI of our temperature measurement results is based on statements made in the calibration certificate of the temperature probe.

First Results for Elemental Natural Hg Vapor at Saturation in Air at Room Temperature. *Isotopic Composition.* It was necessary to ensure that the isotopic composition of the gaseous mercury used in this project was natural. The procedure described above was applied from the sampling sequence to the measurements by ICPMS, with the exception that the solution in syringe 3 was prepared without ERM-AE640. Results from two replicate measurements (Figure S-2 in the Supporting Information) were in agreement within uncertainties with IUPAC values.¹¹ Thus, as a conservative measure because of the rather large uncertainties involved, IUPAC values¹¹ from column 9 were assumed for the isotopic composition of the gaseous mercury in this project and used in the ID-ICPMS calculations.

Mass Concentration. First Hg mass concentration results obtained under room temperature conditions with this measurement procedure are displayed in Figure 2. It represents five replicates (R1 to R5) produced (from air sampling to the

Table 2. Relative Contributions to Combined Uncertainties Estimated for the Hg Mass Concentration Results in This Project ($U = 2.2\text{--}2.8\%$, $k = 2$)

individual sources of uncertainty	contribution to the uncertainty budget		
	individual (%)	combined (%)	origin
Hg amount content in the ERM-AE640	7–11	22–34	external
Hg isotopic composition in the sample (IUPAC)	13–20		
$n(^{200}\text{Hg})/n(^{202}\text{Hg})$ in the ERM-AE639 (for correction for mass discrimination effects)	3–4		
weighing (dilution) of aliquots of ERM-AE640	10–15	64–77	experimental
repeatability of isotope ratio results	1–4		
corrections on intensities during ICPMS measurements	47–66		
other	1–2		

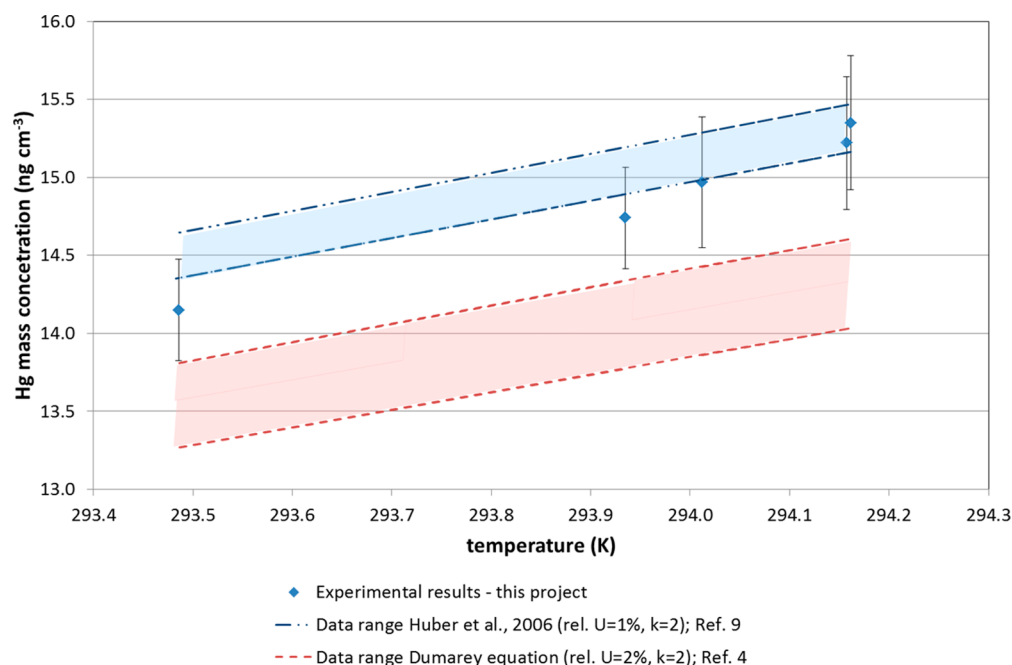


Figure 2. Hg mass concentration results (in ng cm^{-3}) obtained under room temperature conditions in this project. They correspond to five replicates produced on a separate day, over 2 weeks. Vertical bars are expanded combined uncertainty estimations ($k = 2$). For comparison purposes, data corresponding to the Dumarey equation⁴ and values of mass concentrations in air calculated, assuming that the ideal gas law applies, from results of mercury vapor pressure measurements in the presence of only liquid mercury⁹ have also been reported.

mixing stage, sequences 1 to 7) on a separate day, over 2 weeks. ICPMS measurements (sequence 8) were regrouped too, with a first session for R1 to R3 (from week 1) and a second session for R4 and R5 (from week 2). These results correspond to a progression of 1.20 ng cm^{-3} over a range of approximately 0.7°C between 20 and 21°C . The concentrations found (in ng cm^{-3}) are successively 14.15 ± 0.32 , 14.74 ± 0.33 , 14.97 ± 0.42 , 15.22 ± 0.43 , and 15.35 ± 0.43 (for R4, R5, R1, R2, and R3, respectively).

This is on average 5.8% higher than and not in agreement (no overlap within expanded uncertainties) with data calculated from the Dumarey equation under the same temperature conditions. There is however agreement with data derived from vapor correlations proposed by Huber et al.⁹ (-1.2% lower on average).

These first results need to be confirmed, and more experiments are ongoing in particular to check whether similar observations can be made when temperature conditions are changed more drastically. When reviewing what possible source of significant biases could have been overlooked, contamination during the measurement procedure comes first to mind. It seems however that this was not an issue for this procedure under these setup conditions. Procedural blanks were found ($0.099 \pm 0.069 \text{ ng}$ for R1 to R3 and $0.07 + 0.20$ or -0.07 ng for R4 and R5) to represent on average less than 0.1% of the mass of Hg present in 7.4 cm^3 of air. Correcting for these blanks was therefore not an important source of uncertainty.

CONCLUSIONS AND PERSPECTIVES

An innovative procedure was designed to measure the mass concentration of gaseous mercury at saturation in air. The ID-ICPMS based calibration strategy in the liquid phase combined with automated handling of milliliter size air samples under closed circuit conditions are major advantages of this procedure. State of the art chemical metrology principles

were applied that resulted in improvements to procedure validation since the original Dumarey equation experiments were conducted some 30 years ago. Some initial results under room temperature conditions were obtained. They are traceable to the SI in ways that were described. The associated uncertainty that could be estimated from the information currently available ranged, in relative terms, from 2.2% to 2.8% ($k = 2$). The results are not in agreement within stated uncertainties with data calculated from the Dumarey equation. This may of course be due to an underestimation of uncertainty (done posthoc⁴) on data from the Dumarey equation. There is however agreement within stated uncertainties with data reported in Huber et al.⁹

More efforts and developments are necessary to enable measurements with this new procedure under temperature conditions different than ambient. Modifications required include the transfer of the experimental setup to a thermostated chamber. This will be reported in a subsequent paper. The first objective is to investigate the possibility of fitting a new mathematical expression describing the evolution of this Hg concentration as a function of temperature conditions at atmospheric pressure. If the trends described above are confirmed, this could reopen the door to the discussion of the possibility of predicting the mass concentration of gaseous mercury at saturation in air on the basis of mercury vapor pressure correlation data.

ASSOCIATED CONTENT

Supporting Information

Basic premise of the measurement procedure (Figure S-1); results obtained for the measurements of the abundances of the gaseous mercury isotopes used in this project normalized to IUPAC values^{S-1} from column 9 (Figure S-2); Elan 6000 ICPMS parameters (Table S-1); and detailed description of the measurement procedure developed for this project (Table S-2).

This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Brown, A. S.; Brown, R. J. C.; Corns, W. T.; Stockwell, P. B. *Analyst* **2008**, *133*, 946–953.
- (2) Dumarey, R.; Heindryckx, R.; Dams, R.; Hoste, J. *Anal. Chim. Acta* **1979**, *107*, 159–167.
- (3) Dumarey, R.; Temmerman, E.; Dams, R.; Hoste, J. *Anal. Chim. Acta* **1985**, *170*, 337–340.
- (4) Dumarey, R.; Brown, R. J. C.; Corns, W. T.; Brown, A. S.; Stockwell, P. B. *Accred. Qual. Assur.* **2010**, *15*, 409–414.
- (5) Brown, R. J. C.; Brown, A. S.; Yardley, R. E.; Corns, W. T.; Stockwell, P. B. *Atmos. Environ.* **2008**, *42*, 2504–2517.
- (6) ISO. ISO 6978-2:2003 *Natural Gas—Determination of Mercury—Part 2: Sampling of Mercury by Amalgamation on Gold/Platinum Alloy*; International Organization for Standardization: Geneva, Switzerland, 2003.
- (7) ASTM. ASTM D6850-03 *Standard Guide for QC of Screening Methods in Water*; ASTM International, Conshohocken, PA, 2003.
- (8) ISO. ISO 20552:2007 *Workplace Air—Determination of Mercury Vapour—Method Using Gold–Amalgam Collection and Analysis by Atomic Absorption Spectrometry or Atomic Fluorescence Spectrometry*; International Organization for Standardization: Geneva, Switzerland, 2007.
- (9) Huber, M. L.; Laesecke, A.; Friend, D. G. *Ind. Eng. Chem.* **2006**, *45*, 7351–7361.
- (10) Lamberty, A.; Moody, J. R.; van Duffel, E.; De Bièvre, P.; Broothaerts, J.; Taylor, P. D. P.; Lathen, C. *Fresenius J. Anal. Chem.* **1997**, *357*, 359–363.
- (11) Berglund, M.; Wieser, E. *Pure Appl. Chem.* **2011**, *83*, 397–410.
- (12) Nelms, S.; Quétel, C. R.; Prohaska, T.; Taylor, P. J. *Anal. At. Spectrom.* **2001**, *16*, 333–338.
- (13) *Guide to the Expression of Uncertainty in Measurement*; International Organization for Standardization: Geneva, Switzerland, 1995.
- (14) GUM Workbench, *The Software Tool for the Expression of Uncertainty in Measurement*; Metrodata GmbH: Weil am Rhein, Germany, 2003.
- (15) Kragten, J. *Analyst* **1994**, *119*, 2161–2165.
- (16) Quétel, C. R.; Prohaska, T.; Nelms, S.; Diemer, J.; Taylor, P. D. P. *Plasma Source Mass Spectrometry: The New Millennium. In Proceedings of the 7th Durham Conference*; Holland, G., Tanner, S., Eds.; Royal Society of Chemistry: Cambridge, U.K., 2001; pp 257–269.
- (17) Winter, T. G. *Am. J. Phys.* **2003**, *71* (8), 783–786.
- (18) De Bièvre, P. Isotope Dilution Mass Spectrometry (IDMS). In *Trace Element Analysis in Biological Specimens*; Herber, R. F. M., Stoeppler, M., Eds.; Elsevier: Amsterdam, The Netherlands, 1994.

(19) ISO/IEC. *General requirements for the competence of testing and calibration laboratories*, ISO/IEC 17025:2005; International Organization for Standardization/International Electrotechnical Commission: Geneva, Switzerland, 2005.

(20) Hara, N. *Ind. Health* **1975**, *13*, 243–251.

(21) Morita, H.; Mitsuhashi, T.; Sakurai, H.; Shimomura, S. *Anal. Chim. Acta* **1983**, *153*, 351–355.

(22) Ye, Q.; Wang, C.; Wang, D.; Sun, G.; Xu, X. *J. Zhejiang Univ., Sci., B* **2006**, *7* (5), 404–410.

(23) Xu, X.; Ye, Q.; Tang, T.; Wang, D. *J. Hazard. Mater.* **2008**, *158*, 410–416.