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Isotope dilution mass spectrometry as an independent assessment method for mass measurements of milligram quantities of aqueous solution

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ABSTRACT

Isotope dilution mass spectrometry was used to independently assess the accuracy of mass measurement methods developed to quantitatively dispense milligram quantities of aqueous solution. Solutions of isotopically enriched ^{158}Gd and enriched ^{155}Gd were prepared with the molality (mol g^{-1}) of the ^{155}Gd solution being approximately 400 times more dilute than the ^{158}Gd solution. Aliquots of the ^{158}Gd solution were flame sealed in glass ampoules and the ^{155}Gd solution was quantitatively dispensed as a series of 1-g sample aliquots and larger (45 g–55 g) calibration aliquots. Calibration mixes of the solutions were prepared by mass and the Gd isotopic compositions of the ^{155}Gd, ^{158}Gd, and mixed Gd calibration solutions were measured using a high-resolution multi-collector inductively coupled plasma mass spectrometer. These data were used to calculate an elemental amount ratio for Gd in the solutions. Several ^{155}Gd solution sample units were then spiked with small aliquots (0.25 mg–6 mg) of ^{158}Gd solution for which the masses were determined using glass microcapillary and inkjet dispensing methods. The measured Gd isotopic compositions of these mixed solutions, along with the previously calibrated Gd elemental amount ratio and the known masses of the ^{155}Gd aliquots, were used to calculate masses of dispensed ^{158}Gd solution samples. These isotope dilution-based mass measurements have relative expanded uncertainties <0.1% ($k = 2$), which will allow solution masses measured by microcapillary and inkjet dispensing methods to be assessed for accuracy.

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1. Introduction

Isotope dilution mass spectrometry (IDMS) is an established method for measuring amount of an element and, when carefully implemented, can be a primary measurement method that is traceable to the mole [1–3]. The measurements described here represent a novel use of IDMS to precisely quantify the mass[1] of a subsample containing an analyte element rather than the amount of element in a subsample. For this study, the subsamples are milligram-sized aliquots of aqueous solutions. The IDMS-based mass measurements were used to evaluate the accuracy of microbalance mass measurement methods being developed for precise quantification of small solution aliquots. Accurate mass measurements for small solution aliquots are a necessary component of a method currently under development that uses transition-edge-sensor (TES) microcalorimeters for measuring the massic activity of radioactive nuclides [4].

TES microcalorimeters have the potential to perform decay energy spectrometry (DES) with nearly 100% efficiency [4,5]. Additionally, this method can achieve energy resolutions that allow radioactive decays with very similar energies (e.g. ^{239}Pu and ^{240}Pu α decay) to be clearly resolved [6]. These measurements are made by embedding radioactive nuclei in a thermally conductive absorber

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[1] In mass spectrometry the term "mass" is often used as shorthand for atomic mass or molecular weight. The value of mass measured by the IDMS method described in this report is as defined in the International System of Units (SI) from the kilogram base unit and refers to macroscopic mass in this context rather than the atomic or molecular mass. When referring to atomic mass and mass spectrometry, these terms are used specifically in the text.

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where emitted particles and photons are captured and their kinetic energy is converted to thermal energy. The magnitude of this thermal energy is detected by the TES sensors as a proportional increase in temperature of the absorber. Due to the small amount of energy associated with individual decays (in the range of 1 pJ) the resolution of this measurement method is inversely related to the mass of the absorber. For a typical measurement, a sample of a radioactive nuclide in a mineral acid solution (for example nitric acid) might be dispensed onto a 0.015 mm gold foil absorber. To achieve a desirable energy resolution, the foil absorber cannot be much larger than 5 mm^2–10 mm^2. This fact presents a challenge for radioactivity measurements as it is not realistic to dispense more than a few microliters to an absorber of this size.

In practice, radioactivity for most nuclides is measured as massic activity in units of activity per mass of a solvent or a solid matrix (*i.e.,* Bq g^{-1}). To achieve useful measurements of massic activity using TES it will be necessary to quantify the mass of dispensed sample solution to ≤0.1% relative uncertainty for a 95% confidence level. Evaporation of milligram quantities of aqueous solution is rapid under normal laboratory conditions which makes it difficult to precisely measure the mass of the dispensed or received solution. Methods developed to achieve relatively precise mass values for small volumes of dispensed solution include mass-by-difference measurements using disposable "pycnometers" (polyethylene ampoules with drawn out capillary tips) [7,8] or glass microcapillaries [9]. Another method uses an inkjet system to dispense a known number of micro-drops that have been calibrated for mass [10]. Due to size limitations, the pycnometer method is not practical for precise mass measurements of aliquots that are much less than 100 mg. The glass microcapillary and the inkjet dispensing methods are potentially suitable for quantitatively dispensing single milligram solution aliquots but these methods either employ extrapolation from a measured mass to correct for evaporation during measurement (capillary method) or bracketed calibrations of the mass of dispensed drops (inkjet dispenser). Accordingly, there is a need for verification of masses measured by these methods that is independent and sufficiently precise (relative expanded uncertainty ≤0.1%) to identify any significant systematic biases.

For most purposes, liquids can be quantified by volume using graduated cylinders, burettes, volumetric flasks, volumetric pipettes, and analytical pipettes. These methods can be used to dispense milliliter and larger volumes of solution with high precision. If solution density is also known precisely, then a mass of a dispended solution aliquot can be calculated with a relatively small uncertainty. Most of these volumetric devices are not suitable for dispensing microliter volumes of solution necessary for the TES project. For microliter volumes, piston-type analytical pipettes are typically used. These devices can be accurately calibrated by gravimetry for volumes >200 μL and by dye photometric methods for smaller volumes [11]. Despite careful calibration, manufacturers cite accuracy limits of approximately 1% or greater for microliter volumes, even for the most accurate fixed-volume research-grade micropipettes. These volume uncertainties are an order of magnitude too large for verification of masses measured for the TES microcalorimeter project.

Optical microscopy has been used as an independent method to quantify solutions dispensed from an inkjet. This method uses image analysis to measure the diameter of dispensed droplets which, in turn, is used to calculate microdroplet volume [10]. Recent work has demonstrated the ability to determine the volume of dispensed drops with a 0.33% relative uncertainty for a 95% coverage interval [12]. This uncertainty is still 3 times larger than the target uncertainty for the TES project and the uncertainty associated with solution density, necessary for mass calculation, will increase this uncertainty further.

An IDMS-based mass determination method for small solution volumes has the potential to yield results with uncertainties that are small enough to meet the TES project needs (i.e. < 0.1% relative expanded uncertainty). This method does not require any measurement of volume and uncertainty in the density of the solution has minimal influence on measurement precision as solution density is only used for air buoyancy corrections. The IDMS method is also readily scalable across a wide range of sample masses or analyte concentrations. Most importantly, IDMS is largely insensitive to changes in the form or mass of a sample (such as changes due to evaporation) once an isotopic spike has been combined with a sample. Due to these advantages, IDMS measurements can yield accurate, high-precision mass values with relatively small uncertainties. Initial tests using the IDMS mass measurement method, described here, demonstrate the potential for precise determination of small sample masses for verification of more traditional microbalance-based measurements.

2. Theory and methods

2.1. Mass determination by IDMS

Modern multi-collector mass spectrometers are capable of accurately measuring isotope amount ratios on sub microgram quantities of an element with excellent precisions (frequently « 0.1% relative standard deviation). This capability enables precise measurements by IDMS for small amounts of an element or the amount content of an element that occurs as a trace constituent in a bulk matrix material. When the sample being measured and an isotopic spike of known molality can be accurately weighed with a high degree of precision, the measurement resolution for IDMS is generally limited by the uncertainty for the assay of the isotopic spike and/or the uncertainty of mass spectrometric measurements [13] which are often dominated by the uncertainty of calibration standards.

Equation (1) represents an IDMS equation for the molality of a multi-isotope analyte element [14] in solution A (m_A). The analyte element in solution A is relatively enriched in isotope *j*, while solution B contains the same analyte element but is relatively enriched in isotope *i*, depleted in isotope *j*, and has a known molality (m_B). M_A and M_B are the measured masses of aliquots for solutions A and B, and R^{ij} represent isotope amount ratios as measured for solution A, solution B and the IDMS solution mix (AB). X^j is the isotope amount fraction of the specified isotope in each of the 2 solutions.

$$m_A = \frac{m_B M_B}{M_A} \times \left(\frac{R_B^{ij} - R_{AB}^{ij}}{R_{AB}^{ij} - R_A^{ij}} \right) \times \frac{X_B^j}{X_A^j} \quad (1)$$

For this project, M_A is the variable of interest for the IDMS analysis, not m_A. If the molality of the analyte element in both solution A and B are known, M_A can be calculated by a simple rearrangement of Equation (1) (Equation (2)).

$$M_A = \frac{m_B M_B}{m_A} \times \left(\frac{R_B^{ij} - R_{AB}^{ij}}{R_{AB}^{ij} - R_A^{ij}} \right) \times \frac{X_B^j}{X_A^j} \quad (2)$$

To measure M_A with relative expanded uncertainties <0.1%, however, the uncertainty for the molality of the analyte element in both solution A and B must be « 0.1%. It would also be necessary to have small uncertainties for measured isotope amount ratios. This would require, at a minimum, that the known value for the mass spectrometry calibration standard of the analyte element have a

relative uncertainty that is also « 0.1%. Alternatively, a ratio of analyte in the two solutions (R_m) can be determined by measuring the isotopic composition of a calibration mix (ABcal) that was prepared by combining aliquots of solution A and B that have masses (M_{Acal} and M_{Bcal}) large enough to weigh with relatively low uncertainties (<0.05%) (Equation (3)).

$$\frac{M_{Bcal}}{M_{Acal}} \times \left(\frac{R_B^{ij} - R_{ABcal}^{ij}}{R_{ABcal}^{ij} - R_A^{ij}} \right) \times \frac{X_B^j}{X_A^j} = \frac{m_A}{m_B} = R_m \tag{3}$$

R_m can then be substituted into equation (2) (equation (4)) eliminating the necessity of knowing the molality of either solution.

$$M_A = \frac{M_B}{R_m} \times \left(\frac{R_B^{ij} - R_{AB}^{ij}}{R_{AB}^{ij} - R_A^{ij}} \right) \times \frac{X_B^j}{X_A^j} \tag{4}$$

By substituting Equation (3) for the R_m value in Equation (4), it can be seen that the isotope amount-fraction variables factor out of the equation and the remaining variables for calculation of M_A are the masses of calibration aliquots, the mass of the solution B aliquot, and the measured isotope amount ratios for the enriched gadolinium solutions, the calibration solution, and the measured sample (Equation (5)).

$$M_A = \frac{M_B M_{Acal}}{M_{Bcal}} \times \left(\frac{R_B^{ij} - R_{AB}^{ij}}{R_{AB}^{ij} - R_A^{ij}} \right) \times \left(\frac{R_{ABcal}^{ij} - R_A^{ij}}{R_B^{ij} - R_{ABcal}^{ij}} \right) \tag{5}$$

R^{ij} in Equation (5) represents the same isotope amount ratio as measured for 4 different solutions. If these solutions are measured using the same instrument setup and analytical method, then common components of the isotope ratio measurements will factor out of the M_A calculation. For instance, the calculated mass value will be insensitive to collector inter-calibrations and the isotopic composition of the calibration standard used to correct for atomic mass dependent isotope fractionation (i.e. mass bias) because these identical factors are applied to each of the measured ratios. In fact, correcting the isotopic ratio measurements for fractionation is only necessary to compensate for drift of the instrumental fractionation behavior between measurements. Elimination of the uncertainty associated with the isotope amount ratios of calibration standards used to correct for atomic mass dependent isotope fractionation and high precision isotope amount ratio measurements make it possible to determine M_A with a relatively small uncertainty. This uncertainty is limited primarily by the repeatability of the isotopic measurements, and the uncertainties for the mass of the solution B aliquot and the calibration aliquots used to determine R_m.

2.2. Sample and tracer preparation

Nitric acid solutions used for dissolution, dilution, and analysis of samples were prepared from ultra-high purity HNO_3 (Optima, Fisher Scientific Co., Fair Lawn, NJ)[2] and deionized water (18.2 MΩ cm). Sample masses and solution aliquot masses were primarily measured on a calibrated electronic balance that is readable to 0.01 mg (XP205, Mettler-Toledo LLC, Columbus OH). Masses for large dilutions (>100 g) of the experimental solutions were performed on a calibrated Mettler B4 electro-mechanical balance (Mettler-Toledo LLC, Columbus OH). Prior to weighing, laboratory check weights were used to exercise the balances and verify accuracy. All sample weights for this experiment were measured at least twice. Room temperature, relative humidity, and atmospheric pressure were recorded to calculate buoyancy corrections for masses. Masses for solution aliquots of ≤6 g were measured by difference using 5 mL polyethylene pycnometers (Canus Plastic Inc., Ottawa, Ontario). Prior to preparing the solution aliquots, a pycnometer was partially filled with 2.0 mol L^{-1} HNO_3 and weighed 10 times. These replicates were performed to estimate the repeatability of mass measurements for the pycnometers (standard deviation = 0.04 mg). The linearity of the XP205 balance was also checked by comparing the mass of nominal 100 mg and 1 g check weights as measured directly on the balance pan to masses measured by difference (i.e., the mass difference of a 5 g check weight measured with and then without additional 100 mg or 1 g weights). For 3 trials of each check weight, the maximum observed offset of masses measured by difference relative to direct weighing was 0.01 mg for 100 mg and 0.02 mg for 1 g.

Isotopically enriched gadolinium oxides (Gd_2O_3) from the National Isotope Development Center (Oak Ridge, TN) were obtained to prepare “sample” and “tracer” solutions for IDMS analyses. Gadolinium was chosen for 3 primary reasons: 1) reagent and instrument blanks were anticipated to be very low for Gd as well as other lanthanide elements, 2) the oxide is readily soluble in nitric acid, and 3) the isotopes of primary interest for this experiment (^{155}Gd and ^{158}Gd) have only a single, low-abundance elemental isobar (^{158}Dy with $n(^{158}Dy)/n(Dy) = 0.001$ [15]).

Fig. 1 is a schematic showing the various stages of the IDMS mass measurements experiment. A “spike” solution (A) was prepared from (48.5 ± 1.0) mg of ^{158}Gd enriched oxide (lot # 109690) and a concentrated stock of “sample” solution (B) was prepared from (33.7 ± 0.6) mg of ^{155}Gd enriched oxide (lot # 160801). Both enriched gadolinium oxides were transferred to glassine paper that was placed within aluminum weighing pans and then weighed. New, acid-cleaned fluorinated ethylene propylene (FEP) bottles were also weighed. The oxides were transferred to the FEP bottles for dissolution then the bottles and the glassine paper were re-weighed. The received weights for oxide in the bottles were used for estimating the amount of Gd transferred. The oxides were dissolved overnight at room temperature using 10 mL of concentrated Optima HNO_3 and 5 mL of deionized water. No refractory phases or precipitates were observed in either bottle.

The dissolved ^{158}Gd-enriched oxide solution was diluted to a volume of approximately 140 mL with 2.5 mol L^{-1} HNO_3 to produce the final volume of solution A. The solution was shaken vigorously and weighed on the B4 Mettler balance. Then, the cap for the solution bottle was switched for a laboratory squeeze bottle nozzle that was modified with an elongated extension of the dispensing tip. Using this modification, approximately 2 mL of solution A was dispensed directly into the body of 32 cleaned and numbered 2 mL borosilicate glass ampoules. Immediately after filling, the opening of each ampoule was covered with a plastic cap to minimize evaporation until all the ampoules were filled. The ampoules were flame sealed immediately after all the ampoules were filled.

The stock bottle of ^{155}Gd-enriched solution was diluted to a volume of approximately 100 mL, shaken vigorously, and then weighed on the Mettler-Toledo XP205 balance. An aliquot weighing approximately 1.4 g was taken from the stock bottle and transferred to a 500 mL PMP bottle to prepare a diluted solution B for dispensing. The 1.4 g aliquot was diluted with approximately 500 mL of 2.5 mol L^{-1} HNO_3, shaken vigorously, and weighed. A total of 35 sample units were prepared from this volume of solution B. Each unit was contained in a 30 mL high density polyethylene (HDPE) bottle that had been carefully cleaned and then numbered.

[2] Certain commercial equipment, instruments, software, or materials are identified in this paper to foster understanding. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

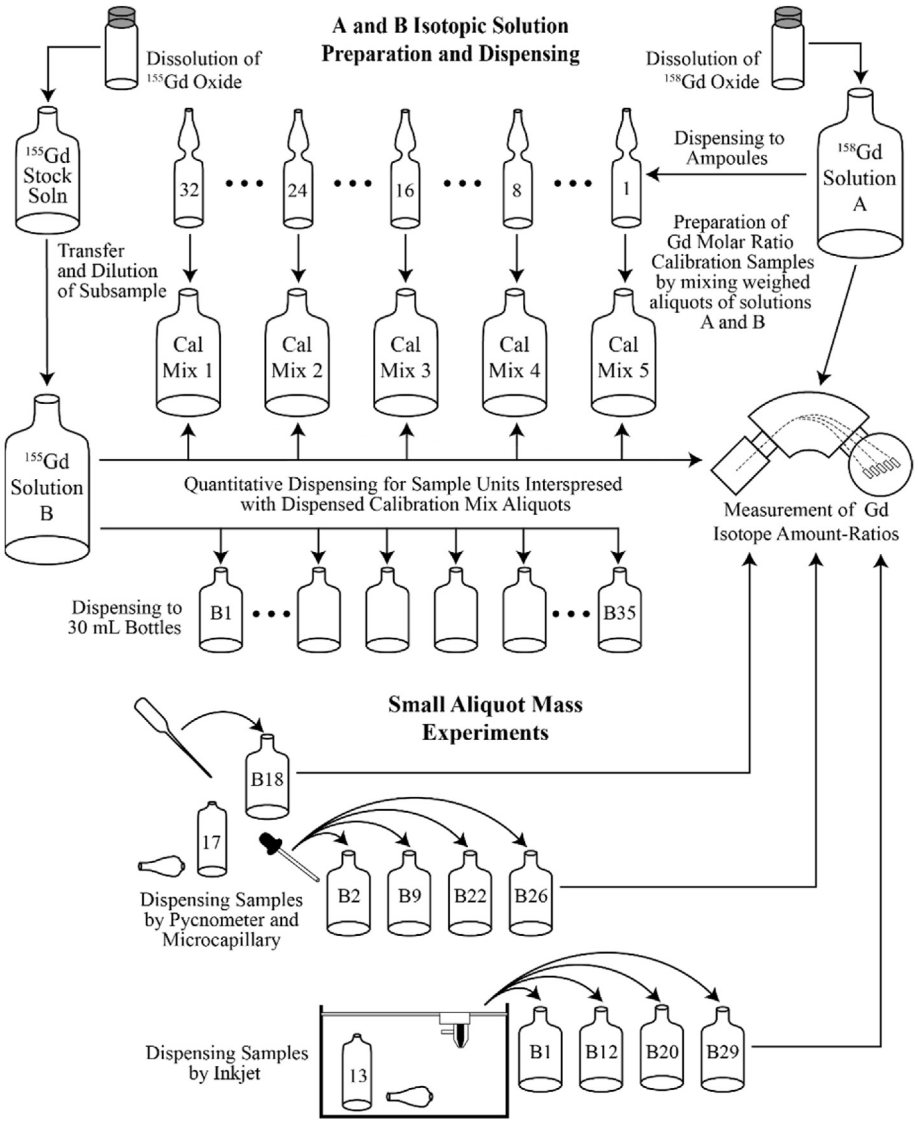

Fig. 1. Mass by IDMS schematic diagram representing the process for the preparation and calibration of gadolinium isotopic solutions and the IDMS measurements of solution aliquots.

Approximately 1 g of solution B was transferred to each bottle with the mass of the aliquot measured by difference using the pycnometer method. A set of 5 calibration samples, ranging from 45 g to 55 g, was also prepared from solution B. These samples were prepared in 60 mL HDPE bottles, that had been cleaned, labeled, and carefully weighed. The solution B was directly dispensed into the bottles which were weighed again. Aliquots for the calibration samples were taken before, after, and interspersed with the dispensing of 1 g sample units to assure that any change in the B solution during preparation of the units would be represented.

A separate ampoule of solution A was opened for each of the 5 solution B calibration samples and aliquots of approximately 0.5 g were transferred from the ampoules to the corresponding solution B calibration sample bottle. The solution A aliquot masses were measured by difference using the pycnometer method. To assure mixing of the solutions, the bottles were capped, shaken, and heated for at least 2 h on hot plate set to 70 °C.

Reverse IDMS analyses were performed to measure the gadolinium molality of the ^{158}Gd enriched solution A and the concentrated ^{155}Gd enriched stock for solution B. Samples for these analyses were prepared by combining a weighed aliquot of each solution with subsamples of a gadolinium SRM solution (SRM 3118a, Lot No. 200511, NIST, Gaithersburg, MD). The measured molality of the stock solution used to prepare solution B was divided by the dilution factor for solution B. The ratio of this value and the measured gadolinium molality for solution A were compared to the R_m value measured for the calibration mixes.

2.3. Small aliquot solution dispensing and weighing

One set of milligram-size solution A samples was prepared using a glass microcapillary dispensing method [9], another set was prepared using an inkjet dispenser method [10], and a single 8 mg control sample was prepared using the pycnometer method. The aliquots dispensed using the glass microcapillary were prepared as outlined in Ref. [9]. Masses for the microcapillary samples were calculated using two different models to correct for evaporation that occurs during handling and weighing of the microcapillary containing solution A. It is beyond the scope of this report to provide detailed explanations of the models, but a summary is

appropriate. The mass for first model (Model 1) was calculated as described in Ref. [9] with two significant modifications. A correction for evaporation of the solution drop during dispensing, referred to as excess evaporation, was not included in the calculation, as the desired value was pre-evaporation mass of dispensed solution rather than the mass of solution when received. Additionally, the timing of the fluid's aspiration into and dispensing from the microcapillary were both noted within 1 s, rendering the temporal variation uncertainty negligible. The Model 1 mass value is based on the difference between the mass of the microcapillary filled with solution and the microcapillary mass after dispensing a portion of the solution. The ultra-microbalance data for both masses is extrapolated to the time of dispensing. The resulting mass for dispensed solution is corrected to a mass equivalent of solution A (prior to evaporation) by estimating a factor for the change in concentration of gadolinium in the solution due to evaporation of the solvent solution. This model assumes that the higher concentration of analyte is uniform throughout the microcapillary at the time of dispensing. The mass for Model 2 is based on the difference between the mass for the full microcapillary extrapolated to the time that the sample solution was aspirated and the mass of the microcapillary, after dispensing, extrapolated to the time of dispensing. This model assumes that all evaporation prior to dispensing occurs from the end of the microcapillary where the solution is dispensed and that any change in concentration is limited to the portion of solution dispensed.

An ampoule of solution A was opened just prior to preparation of the first microcapillary sample aliquot and the opening of the ampoule was carefully covered with Parafilm between aliquots. Solution A was drawn directly from the ampoule into the microcapillary using an eye dropper. The dropper was modified with a rubber septum on the end to hold the microcapillary and a vent hole in the dropper bulb prevented solution from moving within the microcapillary when it was being removed from the septum for weighing. After weighing, the microcapillary was inserted into a 20 μL—200 μL pipette (Mettler-Toledo Rainin LLC, Oakland, CA) that was also modified with a rubber septum on the end and a vent hole in the shaft of the pipettor. The pipettor was used as a plunger to eject a portion of solution from the capillary directly into a solution B unit bottle and not for quantitative dispensing by volume. Weighing of the microcapillary before filling, after filling, and following dispensing was performed on a calibrated Mettler-Toledo XPR 6U ultra-micro balance. Aliquots of solution A, between 2 mg and 6 mg, were dispensed directly into randomly selected units of solution B. To assure mixing after receiving the solution A, the units were tightly capped, shaken, and heated for at least 2 h on a hotplate set at 70 °C.

For the inkjet dispenser samples, a Jetlab 4 tabletop printer (Microfab Technologies, Plano, TX) was used to transfer the solution directly to 4 randomly chosen units of B solution. The burst gravimetry dispensing method and mass calculation used in the study are detailed in Ref. [10]. The reservoir for the dispenser was a 22 mL scintillation vial with a septum cap through which were passed pressure and feed capillaries for the dispenser. Approximately 200 μL of 2 mol L^{-1} HNO_3 was added to the reservoir vial. Then, the solution A ampoule was opened, and the body of the ampoule carefully placed in the bottom of the vial. The feed microcapillary was inserted directly into the solution A within the ampoule and the reservoir vial was sealed with the ampoule completely enclosed. The inkjet dispensing tip was a piezoelectric device with an orifice diameter of 40 μm. The ejection rate (300 Hz) and the regularity of the drops was monitored using a digital camera interfaced with strobe light source. The mass of the drops was calibrated immediately before and after dispensing to the B solution units. The calibration was performed by weighing the mass of a known number of drops (22100 drops totaling approximately 1 mg of solution A) that were dispensed to a tin (Sn) capsule lined with a plastic insert. The capsule was placed directly on the balance pan of a Sartorius SE2 microbalance (Goettingen, Germany) integrated with the inkjet system. During the calibration procedure, the balance pan and the capsule were covered by a cylindrical aluminum draft shield with a 3 mm hole for the dispensed drops to pass through. To help moderate the evaporation rate during calibration, the plastic insert for the Sn capsule was filled with 30 μL of 2 mol L^{-1} HNO_3 prior to being placed on the balance and covered. The capsule weight was monitored until the rate change (due to evaporation) stabilized prior to performing any calibration runs.

A total of 4 test samples were prepared with target masses of 1.0 mg, 0.75 mg, 0.50 mg, and 0.25 mg. This was accomplished by dispensing solution A in 5525-drop bursts, with each unit getting a single 5525-drop burst of solution then, 3 of the units getting a second burst, 2 units getting a third burst, and only a single unit receiving a fourth burst. The B solution units were tightly capped after receiving the A solution and mixing was assured as previously described.

2.4. Mass spectrometry measurements

Gadolinium isotope amount ratio measurements were performed on a Neptune (Thermo Scientific, Waltham, MA) high-resolution multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS). Ion signal intensities were measured on Faraday cups equipped with $1 \bullet 10^{11}$ Ω resistors using the detector configuration and instrument settings shown in Table 1. Samples for isotopic analysis of solution A, solution B, the reverse IDMS samples, and the calibration mix solutions were diluted with 0.5 mol L^{-1} HNO_3 to a gadolinium mass fraction of approximately 100 ng g^{-1}. The samples were introduced to the mass spectrometer through an Aridus II desolvating nebulizer (CETAC Industries, Omaha, NE). Samples for IDMS mass measurement were diluted to 20 ng g^{-1} and a PFA self-aspirating nebulizer (Elemental Scientific, Omaha, NE, USA) connected to a cyclonic/Scott dual spray chamber was used for sample introduction. All measurements were performed using a standard-sample-sample-standard bracketing routine, instrument/analysis blanks were measured before and after each sample analysis, and every measurement was separated by a 60 s rinse cycle. Instrument/analysis blank solutions were comprised of the 0.5 mol L^{-1} HNO_3 solutions that were used to dilute the gadolinium samples and were prepared from the same high-purity HNO_3 and deionized water used to create the sample solutions.

At the beginning of each analysis session, amplifier gain calibrations and mass calibrations were performed and the cup alignment for the gadolinium atomic masses was checked. Mass scans between 148 u and 151 u and between 160 u and 163 u were performed on both the ^{158}Gd enriched solution A and the ^{155}Gd enriched solution B. These scans were to assess the magnitude of any contamination from samarium and dysprosium that could result in isobaric interference and to identify any significant gadolinium hydride formation (i.e $^{160}GdH^+$). No signals for samarium isotopes, dysprosium isotopes, or hydride were observed above background noise for either material. Summed signal intensities for measurements of the A, B, reverse-IDMS, and calibration mix solutions were approximately 25 V. The summed signal intensity for the IDMS mass samples was significantly lower, 1.5 V, due to the lower gadolinium mass fraction of the analysis solutions and declining transmission efficiency for the instrument prior to a major maintenance procedure. A simple mean of instrument/analysis blanks bracketing a sample was subtracted from gain-corrected isotope signal intensities prior to calculation of isotope

Table 1
Neptune MC-ICP-MS instrument setup for gadolinium measurements.

Detector[a]	Low 3	Low 2	Low 1	Center	High 1	High 2	High 3
Isotope	^{152}Gd	^{154}Gd	^{155}Gd	^{156}Gd	^{157}Gd	^{158}Gd	^{160}Gd
Instrument Setup and Analyses Settings: A, B, Reverse-IDMS, and Calibration Solutions							
Sample and Skimmer Cone		Ni cones		Nebulizer		Aridus II	
Guard Electrode		On		- Sample Uptake Rate		100 μL min^{-1}	
Integration Time (s)		4.194		- Ar Sweep Gas Flow Rate		4.75–4.75 L min^{-1}	
Number of Cycles		50		- N_2 Addition Gas Flow rate		0.0–2.0 mL min^{-1}	
RF Power (W)		1215		- Spray Chamber Temp		110 °C	
Instrument Analysis Gas		Ar		- Membrane Oven Temp		160 °C	
- Coolant Gas Flow Rate		16 L min^{-1}					
- Sample Gas Flow Rate		1.01 L min^{-1}					
- Auxiliary Gas Flow Rate		0.96 L min^{-1}					
Instrument Setup and Analyses Settings: IDMS Mass Measurement Samples							
Sample and Skimmer Cone		Al cones		Nebulizer		Elemental PFA	
Guard Electrode		On		- Sample Uptake Rate		400 μL min^{-1}	
Integration Time (s)		4.194					
Number of Cycles		50					
RF Power (W)		1215					
Instrument Analysis Gas		Ar					
- Coolant Gas Flow Rate		16 L min^{-1}					
- Sample Gas Flow Rate		1.125 L min^{-1}					
- Auxiliary Gas Flow Rate		1.01 L min^{-1}					

[a] Configuration of Faraday cup detectors for gadolinium measurements.

ratios. A gadolinium standard solution of SRM 3118a was diluted to the same concentration as the analysis samples (i.e., 100 ng g^{-1} and 20 ng g^{-1}) and was measured for instrument calibration. IUPAC values for representative isotopic abundances of gadolinium [15] were assumed and the measured $n(^{156}\text{Gd})/n(^{158}\text{Gd})$ ratio of the of SRM 3118a was used to calculate correction factors (exponential law) for the measured isotope amount ratios to compensate for atomic mass dependent isotope fractionation. The correction factors applied to the sample data were mean values determined from SRM analyses bracketing each sample (weighted by temporal proximity to sample being corrected) and were applied primary to compensate for any drift in instrumental fractionation behavior. In total, 6 replicate measurements were made for both the A and B solutions; all other samples were analyzed in duplicate.

3. Results

3.1. Isotope amount ratios for enriched gadolinium solutions

The measured isotope amount ratios of gadolinium in the A and B solutions are provided in Table 2. The measured isotopic compositions are consistent with the values provided by the vendor for the ^{158}Gd enriched oxide ($n(^{158}\text{Gd})/n(\text{Gd}) = 0.975(1)$) and the ^{155}Gd enriched oxide ($n(^{158}\text{Gd})/n(\text{Gd}) = 0.0094(5)$). Instrument/analysis blanks ranged from a low of 0.02 mV at atomic mass 152 u during the B solution analysis session up to 4.4 mV at atomic mass 158 u during analysis of the A solution. The standard deviations of the measured blank signal intensities for each session were used to estimate uncertainties for blank corrections, which represent the dominant uncertainty component for most of the measured isotope ratios. The standard uncertainties of replicate measurements and the uncertainty of the IUPAC-derived $n(^{156}\text{Gd})/n(^{158}\text{Gd})$ ratio used for the mass bias correction are significant uncertainty components only for the more abundant isotopes in each material (i.e., amount fractions >0.01).

3.2. Elemental ratio for enriched gadolinium solutions

Measurement data for determining the ratio of gadolinium amount content in the A and B solution (R_m) and data for verification measurements by IDMS are provided in Table 3. The uncertainties for the R_m values are dominated by the uncertainty component for the repeatability of the measured $n(^{155}\text{Gd})/n(^{158}\text{Gd})$ ratios. The uncertainty for the combined (mean) R_m also includes the standard deviation of 0.064 mol mol^{-1} for the 5 measured calibration samples. The verification value for R_m calculated using reverse IDMS measurements of the enriched solutions is consistent with the high precision value determined from the calibration mixes.

3.3. Solution mass determinations by IDMS

The results for the mass measurements by IDMS are provided in Table 4. Fig. 2 shows the relative deviation of the aliquot masses, as measured during dispensing, from those determined by IDMS. The relative expanded uncertainties for the IDMS-based masses range from 0.06% to 0.09%. The uncertainty for IDMS masses is primarily due to the uncertainty of the calibrated R_m ratio and the variability of the mass spectrometry measurements (Table 5). The measured $n(^{155}\text{Gd})/n(^{158}\text{Gd})$ ratios for the enriched solutions and the mass of

Table 2
Isotope amount Ratios and Isotope Amount Fractions for Enriched Gd.

Isotope amount Ratio	Solution A[a]	Solution B[a]
$n(^{152}\text{Gd})/n(^{158}\text{Gd})$	0.00003797 (68)	0.011178 (85)
$n(^{154}\text{Gd})/n(^{158}\text{Gd})$	0.0003660 (43)	0.6514 (32)
$n(^{155}\text{Gd})/n(^{158}\text{Gd})$	**0.002567 (34)** [b]	**95.32 (57)** [b]
$n(^{156}\text{Gd})/n(^{158}\text{Gd})$	0.005622 (42)	5.373 (26)
$n(^{157}\text{Gd})/n(^{158}\text{Gd})$	0.008102 (40)	1.1932 (66)
$n(^{158}\text{Gd})/n(^{158}\text{Gd})$	1.000000 (00)	1.00000 (00)
$n(^{160}\text{Gd})/n(^{158}\text{Gd})$	0.008514 (35)	0.4329 (47)
Isotope amount Fraction	**Solution A**	**Solution B**
$n(^{158}\text{Gd})/n(\text{Gd})$	**0.97541 (10)** [b]	**0.009617 (56)** [b]

[a] Expanded uncertainties (U) are in parenthesis and correspond to the last digits of the reported values. Expanded uncertainties are the product of the combined standard uncertainty (u_c) and a coverage factor (k) of 2 for an approximately 95% level of confidence. Values and uncertainties, consistent with international protocols [16,17], were calculated using GUM WorkBench Software (Metrodata GmbH, Braunschweig, Germany).

[b] Values in boldface were used for the calculation of IDMS-based masses and/or R_m.

Table 3
Calibration data for Molar ratio of gadolinium in solutions A and B.

Solution A Ampoule No.	Aliquot Mass[a] (g)	Solution B Aliquot	Aliquot Mass[a] (g)	Measured $n(^{155}Gd)/n(^{158}Gd)$	R_m (mol mol^{-1})
32	0.46116 (06)	Cal 1	50.9012 (24)	0.25352 (10)	412.26 (21)
24	0.47300 (07)	Cal 2	46.4059 (23)	0.22565 (09)	412.34 (21)
16	0.55956 (07)	Cal 3	54.0454 (24)	0.22225 (11)	412.24 (24)
8	0.46156 (08)	Cal 4	49.9514 (24)	0.24868 (11)	412.18 (23)
1	0.60765 (08)	Cal 5	54.3406 (24)	0.20596 (08)	412.31 (21)
Combined R_m Value for Calibration Mixes (mol mol^{-1})					412.27 (24)
IDMS Sample	**Sample Aliquot Mass (g)**	**Dilution Factor**	**SRM Aliquot Mass (g)[c]**	**Measured $n(^{156}Gd)/n(^{158}Gd)$**	***Molality*** **(μmol g^{-1})**
Solution A	6.09380 (16)	–	0.27150 (6)	0.227031 (91)	1.9379 (79)
Stock B[b]	4.96625 (15)	376.208 (21)	0.11506 (7)	1.02742 (41)	1.787 (32)
Verification R_m Value from Reverse IDMS Measurements (mol mol^{-1})					407.9 (8.1)

[a] Solution aliquots were weighed on a 5-place balance and were corrected for air buoyancy based on laboratory conditions at the time of weighing.
[b] Measured molality of the stock for solution B was divided by the cited dilution factor to calculate the verification value for R_m.
[c] Molality of the diluted SRM 3118a solution used as a reverse spike was 63.34 (21) μmol g^{-1}.

Table 4
Solution aliquot mass measurements by IDMS data.

B Solution Unit	Aliquot Mass (g)	A Solution Dispensing[a]	Measured $n(^{155}Gd)/n(^{158}Gd)$	IDMS-Based Mass (mg)	Weighed[b] Mass (mg)
18	1.05340 (13)	pycnometer	0.27615 (10)	8.7520 (56)	8.748 (46)
2	1.05727 (11)	micro- capillary	0.59954 (33)	4.0119 (31)	4.0110 (50)
					4.0142 (34)
9	1.07633 (12)		0.56429 (22)	4.3422 (29)	4.3402 (38)
					4.3433 (28)
22	1.17639 (11)		0.51952 (19)	5.1593 (34)	5.1480 (67)
					5.1514 (53)
26	1.10209 (12)		0.46855 (24)	5.3650 (40)	5.3643 (39)
					5.3680 (31)
1	1.09857 (11)	Inkjet dispenser	2.3552 (16)	1.03367 (92)	1.0246 (24)
12	0.97747 (10)		2.8921 (08)	0.74776 (48)	0.7685 (18)
20	1.06772 (11)		4.4917 (17)	0.51664 (38)	0.5123 (12)
29	1.06872 (11)		8.5831 (29)	0.25836 (23)	0.2562 (06)

[a] The solution A aliquots for the pycnometer and microcapillary samples were taken from ampoule 17. Inkjet samples were from ampoule 13.
[b] Two mass values are listed for each microcapillary sample in this column. The first value is the Model 1 value and the second is the Model 2 value as described in Section 2.3.

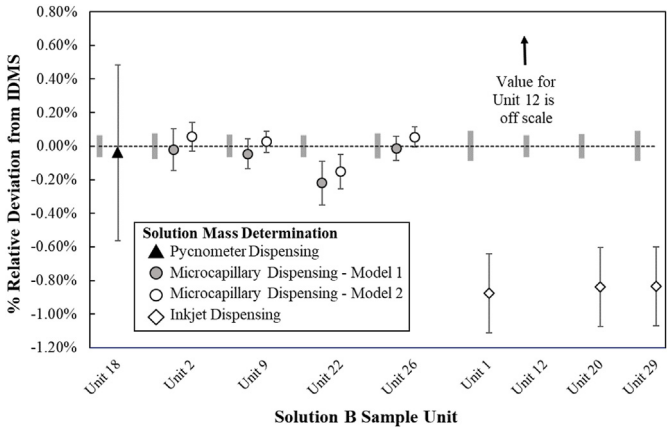

Fig. 2. Relative difference between solution A aliquot masses measured by IDMS and masses measured by indicated methods. Gray bars on the dashed zero-line show the relative uncertainty interval for IDMS mass measurements of each sample. All error bars represent expanded uncertainties ($k = 2$).

the solution B aliquots are minor contributors to the measurement uncertainty except for the "under-spiked" 0.5 mg and 0.25 mg inkjet dispensed samples for which the uncertainty of the measured $(^{155}Gd)/n(^{158}Gd)$ ratio of solution B contributes significantly.

The mass for the control aliquot dispensed by pycnometer is consistent with the mass measured by IDMS. The two different mass value models for the microcapillary measurements are also equivalent, within uncertainties, to the IDMS values except for the aliquot dispensed into solution B unit 22. The relative difference between the IDMS and the Model 1 microcapillary mass for this sample is 0.22%. It is notable that the full microcapillary for this sample was inadvertently weighed for more than twice the duration (160 s) of the other microcapillary weighings (approximately 60 s). Furthermore, the balance response during weighing was unusual with oscillating mass readings rather than the uniform decrease that would be expected to result from evaporation.

The masses for the inkjet dispensed aliquots show a consistent bias relative to IDMS masses, with the values calculated using the calibrated drops being 0.84%–0.88% lower for aliquots dispensed to solution B units 1, 20, and 29. The inkjet mass value for unit 12 is 2.8% higher than the IDMS mass value, which is a significant deviation from both the magnitude and direction of difference for the other measurement. Except for this aliquot, the proportions of the masses measured by IDMS data are consistent with expectations based on the number of drops dispensed to each unit. The ratio of IDMS measured mass for the nominal 0.5 mg sample to the 1.0 mg sample is 0.4998 and the ratio of the nominal 0.25 mg sample to the 1.0 mg sample is 0.2499.

4. Discussion

The isotope amount ratio measurements that are critical to the IDMS-based mass determinations were normalized using measurements of SRM 3118a. This SRM is certified for mass fraction of gadolinium but not for isotopic composition. Instead, the isotopic composition and uncertainties for natural gadolinium, as reported in Ref. [15], were assumed for this material. Use of this SRM and

Table 5
Example uncertainty budget for IDMS mass measurement[a].

Uncertainty Component	Description	Assessment Type	Relative standard uncertainty (%) of contributing component
M_{Acal}	Mass of solution A aliquots for R_m calibration	B	0.005
M_{Bcal}	Mass of solution B aliquots for R_m calibration	B	0.002
R^{ij}_{ABcal}	Measured $n(^{155}Gd)/n(^{158}Gd)$ for R_m calibration	A	0.021
δ_{VarCal}	Variability of replicate R_m calibrations	A	0.016
M_B	Mass of solution B aliquot for measurement	B	0.005
R^{ij}_A	Measured $n(^{155}Gd)/n(^{158}Gd)$ in A solution	B	0.007
R^{ij}_B	Measured $n(^{155}Gd)/n(^{158}Gd)$ in B solution	B	0.007
R^{ij}_{AB}	Measured $n(^{155}Gd)/n(^{158}Gd)$ in IDMS solution	A	0.034
M_A	**Relative combined standard uncertainty (%)**		**0.045**

[a] Uncertainty budget shown here is for the nominal 1 mg sample dispensed by inkjet to solution B unit 1.

assuming a natural isotopic composition represents a significant limitation for measuring gadolinium isotopic composition on an absolute basis. A gadolinium certified isotopic reference material has recently been developed with relative expanded uncertainties ($k = 2$) of ≤0.1% for isotope amount ratios [18]. Use of this CRM could bolster the traceability of the isotopic measurements reported but would not improve the precision of the mass by IDMS technique. The isotopic measurement data for the mass measurement serve as a mechanism for linking measurements of relatively large solution masses (i.e., R_m calibration) to much smaller masses. As discussed previously, the results are highly dependent on mass spectrometric data that are measured and normalized in a consistent manner but are insensitive to differences between the assumed and true values of the calibrant material used for normalization.

The pycnometer method has been extensively used for quantitative dispensing of aqueous solutions. Accordingly, this method was used to demonstrate the accuracy of the mass by IDMS method by dispensing a small 8.748(46) mg control sample of solution A. The large uncertainty for the pycnometer measurement (0.52% relative, $k = 2$), however, highlights the limitations of this method for milligram-size solution aliquots.

Both models for the Solution A mass determined by the microcapillary dispensing method were within uncertainties of one another as well as the mass as determined by the IDMS method (except unit 22). The small systematic difference observed between the Model 1 and Model 2 masses is the result of the different assumptions about the concentration of analyte remaining in the microcapillary after dispensing. Neither of these models represents a detailed characterization of changes in the amount of dispensed analyte due to evaporation of the carrier solution. Considering the estimated diffusion coefficient of gadolinium in nitric acid ($1.23 \bullet 10^{-9}$ m^2 s^{-1} [19]) it is improbable that the concentration of gadolinium in the microcapillary will equilibrate throughout the microcapillary as the solution evaporates (Model 1). It is also unlikely that all evaporation would be localized to one end of the microcapillary or that no mechanical mixing will occur during dispensing of the solution (Model 2). Instead, these models are end member conditions for the dispensing method and the resulting difference in calculated values represents the limit of resolution for the measured mass values. Despite the limitation resulting from the evaporation corrections, the observation that both model values are quite close to the IDMS-based values demonstrates that 0.1% relative uncertainties are reasonable for milligram size aliquots using the microcapillary method.

The mass of solution A measured for unit 22 using the microcapillary weighing method showed a clear bias relative the IDMS method. The longer weighing time for this sample could have resulted in more extensive evaporation during the preparation thus amplifying any biases in the mass calculation for the microcapillary method. Alternatively, the unusual behavior observed in the balance data for this weighing may have skewed the extrapolated mass for the full microcapillary. Regardless of the cause, the IDMS mass measurement was able to demonstrate that anomalous conditions for aliquots weighed using the microcapillary method have significant effects on the resulting mass calculations.

The systematically lower masses for calibrated inkjet dispensed solution were not unexpected. The dispenser calibration technique was developed to determine the mass of a solution deposited to a surface and not the equivalent mass of a reservoir solution prior to evaporation that occurs during dispensing. For the IDMS samples, the dispenser tip was greater than 20 mm from the reservoir of solution in the capsule used to calibrate drop masses, the diameter of dispensed drops was approximately 44 μm, and the initial velocity of the drops was less than 2.0 m s^{-1}. Trost [20] performed a detailed study of variables affecting mass measurement of inkjet dispensed fluids using a dispenser system that is nearly identical to the system used in this study. He calculated that a 60 μm diameter drop of water falling 28 mm with an initial velocity 4 m s^{-1} would lose between 0.81% and 1.48% of its mass. Considering these model estimates, the 0.8%–0.9% mass loss observed for 2 mol L^{-1} HNO_3 solution A is reasonable for the dispensing conditions of the IDMS experiment.

It is difficult to definitively identify a cause for the 2.8% higher inkjet mass value of solution dispensed to unit 12 relative to the IDMS-based mass. Possible explanations include: 1) an error in the measured mass of solution B receiving the solution A spike; 2) transient failure of the dispenser, and 3) loss of material between the dispenser and the sample solution. Records from preparation of the solution B units were review, and it was determined that the dispensed and received masses measured for unit 12 differ by only −0.03% (consistent with a small proportion of evaporation during transfer). Therefore, an error in the measured mass of solution B is unlikely as a cause for the discrepancy. Solution A was dispensed to this unit in three bursts with solution being dispensed to other units both before and after all bursts to this sample unit. The inkjet samples masses are consistent with expected values for the other 3 samples, so a failure of the inkjet dispenser being a cause for the anomalous IDMS data appears unlikely but cannot be categorically ruled out. A more likely cause for the bias is that some proportion of the dispensed drops did not get incorporated into the solution B unit. During transfer of solution A, the tip of the dispenser was several mm above the rim of the solution B sample bottle which has a 28 mm diameter opening. Transient air currents or electrostatic effects could plausibly result in some of the aerosolized 45 ng spike drops being deposited somewhere other than the interior of the sample bottle.

It is notable that inkjet system used for this experiment was not optimized to minimize evaporation during dispensing. It is anticipated that improvements being incorporated into the methodology will significantly improve accuracy of drop mass calibrations. These include changes to the calibration procedure such as reducing the

height of the aluminum draft shield, increasing the volume of solution in the calibration capsules, and setting the dispenser orifice within the opening of the draft shield, thereby significantly reducing the travel distance for solution drops. Changes to dispensing parameters such as drop size and velocity may also be incorporated to reduce the surface area and duration for potential evaporation. The same improvements (proximity to sample container, larger drop size, greater dispensed velocity) can also reduce the potential for sample loss. Additional mass measurements by IDMS and a separate set of tests measurements using a ^{241}Am solution and liquid scintillation counting (LSC) will be used to assess the success of these changes and, if necessary, establish an evaporation correction factor for the inkjet dispenser calibration.

The IDMS determinations performed for this project show the potential for high precision mass measurements of sample matrix. This method, however, is not easily adaptable for routine weighing. IDMS requires the addition of an isotopic spike to the matrix being weighed, which could interfere with the experiment for which the sample is being prepared. IDMS is a destructive analysis method requiring that, at minimum, a portion of the spiked sample is consumed. Also, the IDMS method is relatively time consuming and resource intensive compared to other methods for measuring mass. Due to these factors, mass determination by IDMS is not realistic for routine analysis but is a valuable tool for precisely validating and/or calibrating mass measurement methods in circumstances where verification by other methods is impractical.

5. Conclusion

Methods for dispensing and measuring the mass of milligram size solution aliquots, such as the microcapillary and inkjet dispenser methods, show promise but need to be validated. The IDMS-based mass measurement technique demonstrated in this study produced results that are consistent with weighing by difference using highly sensitive modern electronic balances and produced results with relative expanded measurement uncertainties of less than 0.1%. Therefore, this method can be used as an independent check of developing mass measurements for small quantities of dispensed solution. More importantly, the method has sufficient resolution to allow for the recognition of relatively small ($\approx$0.1%) biases in measurement techniques or weighing errors due to issues with the measurement procedures.

Author statement

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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