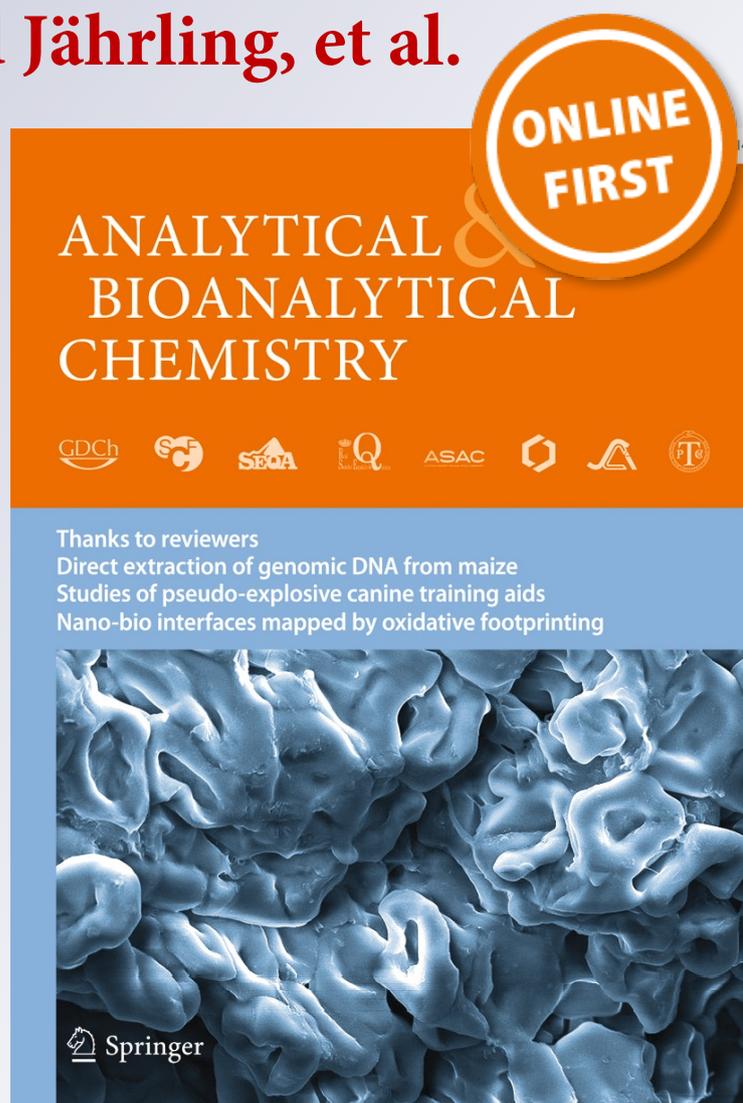# Gravimetric preparation and characterization of primary reference solutions of molybdenum and rhodium

Angela Kaltenbach, Janine Noordmann, Volker Görlitz, Carola Pape, Silke Richter, Heinrich Kipphardt, Gernot Kopp, Reinhard Jährling, et al.

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Gravimetric preparation and characterization of primary reference solutions of molybdenum and rhodium

Angela Kaltenbach · Janine Noordmann · Volker Görlitz · Carola Pape ·
Silke Richter · Heinrich Kipphardt · Gernot Kopp · Reinhard Jährling ·
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Abstract Gravimetrically prepared mono-elemental reference solutions having a well-known mass fraction of approximately 1 g/kg (or a mass concentration of 1 g/L) define the very basis of virtually all measurements in inorganic analysis. Serving as the starting materials of all standard/calibration solutions, they link virtually all measurements of inorganic analytes (regardless of the method applied) to the purity of the solid materials (high-purity metals or salts) they were prepared from. In case these solid materials are characterized comprehensively with respect to their purity, this link also establishes direct metrological traceability to *The International System of Units* (SI). This, in turn, ensures the comparability of all results on the highest level achievable. Several national metrology institutes (NMIs) and designated institutes (DIs) have been working for nearly two decades in close cooperation with commercial producers on making an increasing number of traceable reference solutions available. Besides the comprehensive characterization of the solid starting materials, dissolving them both loss-free and completely under strict gravimetric control is a challenging problem in the case of several elements like molybdenum and rhodium. Within the framework of the *European Metrology Research Programme* (EMRP), in the *Joint Research Project* (JRP) called SIB09

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Primary standards for challenging elements, reference solutions of molybdenum and rhodium were prepared directly from the respective metals with a relative expanded uncertainty associated with the mass fraction of $U_{rel}(w) < 0.05$ %. To achieve this, a microwave-assisted digestion procedure for Rh and a hotplate digestion procedure for Mo were developed along with highly accurate and precise inductively coupled plasma optical emission spectrometry (ICP OES) and multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS) methods required to assist with the preparation and as dissemination tools.

Introduction

The most elegant and conclusive way to achieve comparable measurement results or to render such results suitable for acceptance in law suits is to establish so-called *metrological traceability* [1]. The basic concept of metrological traceability is the establishment of an unbroken chain of calibrations, each contributing to the measurement uncertainty, to relate a measurement result to a reference, which at best is the realization of the SI unit [2, 3]. Large areas of analytical chemistry are concerned with the measurement of the contents of, e.g., precious, poisonous, or essential elements in a wide variety of sample matrices, with applications in environmental protection, health care, industrial production, etc., whenever limits or contents are legally and/or, often as a consequence, economically important or, e.g., when the health of human beings is at stake. In elemental analysis, worldwide attempts are underway to establish a calibration hierarchy for mono-elemental solutions [4–9] because these solutions with their well-known element contents are required for every kind of

inorganic analysis, no matter what analytical method is applied. In the end, virtually all methods from AAS, to inductively coupled plasma optical emission spectrometry (ICP OES) and ICP MS, and to isotope dilution techniques rely on an elemental calibration solution. These usually commercially available solutions need to have a well-known content to yield comparable and accurate results. A prerequisite for the traceability of these solutions to the SI is the availability of so-called primary solutions prepared according to the highest metrological standards resulting in the lowest possible uncertainty associated with their element contents. Therefore, the primary solutions have to be prepared gravimetrically and loss-free directly, e.g., from pure metals with exactly known purity (including well-known metallic and non-metallic impurities) [8] and every weight measured on the way from the starting material to the final solution needs to be air buoyancy-corrected. These primary solutions are then used to link up the commercial solutions to ensure the comparability of "everyday" results determined in laboratories all over the world.

Rhodium and molybdenum are relatively precious and a lot of important technical applications rely on well-known contents. However, currently available primary solutions (like NIST SRM 3144 and 3134, respectively) are either prepared from salts or metal powders with an unknown and hard to clean surface (in the case of Rh [10]) or the matrices of the primary solution and the commercially available solutions do not match (in the case of Mo). Preparing a primary solution from a salt can result in a mass fraction that deviates from the theoretically calculated value, if the stoichiometry is not verified. Additionally, the relative expanded uncertainty of the mass fraction of those solutions is larger than the target uncertainty of 0.1 % for primary solutions. This uncertainty is vital for transfer standards, as a target uncertainty of 0.3 % for the calibration of commercial solutions should be obtained. Thus, primary solutions of molybdenum and rhodium were prepared in the framework of the *European Metrology Research Programme* (EMRP), within the *Joint Research Project* (JRP) called SIB09 *Primary standards for challenging elements*. To accomplish this, at the same time, contamination- and loss-free as well as quantitative procedures to bring these pure solid metals directly into solution had to be developed; in the case of rhodium, for the first time starting from the metal itself with a defined surface that was easy to clean. Additionally, the solutions match the matrix of the commercially available products, which eliminates matrix effects during the calibration of commercial solutions, resulting at least in a lower measurement uncertainty.

Both ICP OES and multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS) are commonly recognized as achieving highly precise and accurate measurement results in elemental analysis, especially when sophisticated measurement regimes like bracketing combined with an internal standard (IS) are applied [11–14, 7, 15]. Therefore, these techniques were applied not only to develop methods for

the linkup of commercial solutions to the primary solutions but also to validate the repeatability of the dissolution and storage procedures as well as to ensure the completeness of the dissolution and the absence of losses.

Experimental

Molybdenum solution Molybdenum rods (3 mm diameter, 99.95 %, Alfa Aesar GmbH, Germany, lot F05F20) were cut into pieces of approximately 1 g (14 mm) each. The surface of the pieces was cleaned using an etching procedure, in accordance with the recipe for the determination of impurities in the solid metal [8]. Briefly, the molybdenum rods were placed into a mixture of 4 mL nitric acid ($w(HNO_3)$=0.65 g/g, sub-boiled) and 1 mL hydrofluoric acid ($w(HF)$=0.40 g/g, ultrapur, Merck KGaA, Germany) for 10 s, then they were rinsed with water ($\sigma <$ 0.066 µS/cm, Milli-Q Element A10, EMD Millipore Corporation, USA), etched with hydrochloric acid ($w(HCl)$= 0.32 g/g, ultrapur, Merck KGaA, Germany), again cleaned with water, and then treated with ethanol (p. A., Merck KGaA, Germany) in an ultrasonic bath. The last two steps were repeated three times. After weighing 2 g (air buoyancy-corrected mass) of molybdenum (2 pieces) directly into a pre-cleaned and blank-checked DURAN® bottle (Schott AG, Germany), 30 g of nitric acid ($w(HNO_3)$=0.30 g/g) were added to dissolve the sample within 6 h using a heating block on a hotplate (120 °C hotplate temperature). Afterwards, the solution was evaporated to dryness and the sample was allowed to cool down to room temperature. Then, 50 g of ammonium hydroxide ($w(NH_3)$=0.25 g/g, ultrapur, Merck KGaA, Germany) were added to the residue and heated again on the hotplate (parameters as before) for 3 h to ensure complete dissolution. The resulting clear solution was evaporated to dryness and water was added to the residue to adjust a molybdenum mass fraction of $w(Mo) \approx 4$ g/kg. This stock solution was diluted gravimetrically to yield several 500 g aliquots of the desired $w(Mo)$=1 g/kg solution.

Rhodium solution Rhodium foil (thickness 0.025 mm, 99.8 %, Alfa Aesar GmbH, Germany, lot MM48317) was cut into pieces of approximately 100 mg each. The pieces were cleaned using an ultrasonic bath for 1 min each utilizing acetone (SupraSolv®, Merck KGaA, Germany), nitric acid ($n(HNO_3)/m$=0.15 mol/kg), water ($\sigma <$0.066 µS/cm, Milli-Q Element A10, EMD Millipore Corporation, USA), and again acetone, respectively. After drying in a clean environment at room temperature, one piece each was weighed directly into four thoroughly pre-cleaned and blank-checked 35 mL quartz vessels (MLS GmbH, Germany). About 15 mL hydrochloric acid ($w(HCl)$=0.32 g/g, ultrapur, Merck KGaA, Germany) and 3 mL hydrogen peroxide ($w(H_2O_2)$=0.31 g/g, ultrapur, Merck KGaA, Germany) were then added to each vessel. After attaching PTFE caps featuring pressure release holes, the

vessels were placed in a microwave autoclave (turboWAVE, MLS GmbH, Germany). At room temperature, a base pressure of 50 bar was applied to the autoclave using argon (5.0, Linde, Germany). Following this, the samples were heated, microwave-assisted, to 260 °C (≤105 bar) within 15 min. After holding this temperature for another 50 min, the samples were allowed to cool down to 35 °C within 30 min. Finally, the remaining pressure was released at a rate of 5 bar/min. The vessels were then placed on a hotplate and the rhodium solution was evaporated to near dryness within 6 h applying a hotplate surface temperature of 130 °C. One milliliter sub-boiled nitric acid (prepared from $w(HNO_3)=0.65$ g/g, EMSURE® ISO using a Cetac OmniPure, Teledyne Technologies Inc., USA) was added. After evaporation to near dryness, the residues were redissolved in sub-boiled nitric acid ($w(HNO_3)=0.025$ g/g) and homogenization was achieved by placing the vessels in an ultrasonic bath heated to 70 °C for about 4 h. Finally, the solutions were transferred into a thoroughly pre-cleaned and blank-checked 500-mL PFA bottle (AHF analysentechnik, Germany). The air buoyancy-corrected mass of the PFA bottle had been determined beforehand. A suitable amount of nitric acid ($w(HNO_3)=0.025$ g/g) was added to result in approximately 500 g of a solution with a rhodium mass fraction of $w(Rh)\approx$ 1.5 g/kg. Several of these stock solutions were prepared and diluted gravimetrically to yield a corresponding number of 500 g aliquots of the desired 1 g/kg solution.

Mass fractions of molybdenum and rhodium and their associated uncertainties All mass fractions were calculated from the evaporation correction/sampling scheme applied to the solutions (Fig. 1). Provided a suitable bottle material and an appropriate solvent and, thus, a stable chemical form of the element was chosen in preliminary experiments, the mass fraction of the element in the solution is a function of time and changes due to evaporation losses during storage. To correct for these losses, not only the mass of the remaining solution has to be determined prior to taking an aliquot from the bottle but also the remaining mass immediately after the sampling (and prior to the next storage stage). First of all, the empty bottle was weighed on a balance (B) with a mass resolution of $\Delta m=0.01$ mg (MC210S, Sartorius AG, Germany) and at the same time (1) on the balance (A) intended for the weighing of the final solution ($\Delta m=0.1$ mg, H315, Mettler Instrumente AG, Switzerland). Additionally, the ambient conditions (temperature ϑ_1, relative humidity φ_1, and pressure p_1 of the air) were determined using a corresponding gauge (testo 650 with sensors 0638.1645 and 0636.9741, Testo GmbH & Co, Germany) to correct for the air buoyancy. This was accomplished by applying an air buoyancy correction factor K to all readings m' from the balances to calculate the actual mass m:

$$m = K \times m'\tag{1}$$

The air buoyancy correction factor of a certain object weighed on a balance is a function of the object's density ρ_i, the density of the traceable weights used to calibrate the balance ρ_{cal}, and of the air density ρ_{air}, which, in turn, is a function of the ambient conditions [16–18]:

$$K_i = \frac{\left(1-\dfrac{\rho_{air}}{\rho_{cal}}\right)}{\left(1-\dfrac{\rho_{air}}{\rho_i}\right)}\tag{2}$$

$$\rho_{air} = \frac{0.348444\,\frac{kg/m^3}{hPa}\times p - \phi \times \left(0.252\,\frac{kg/m^3}{°C}\times\vartheta - 2.0582\,\frac{kg}{m^3}\right)}{273.15+\vartheta/°C}\tag{3}$$
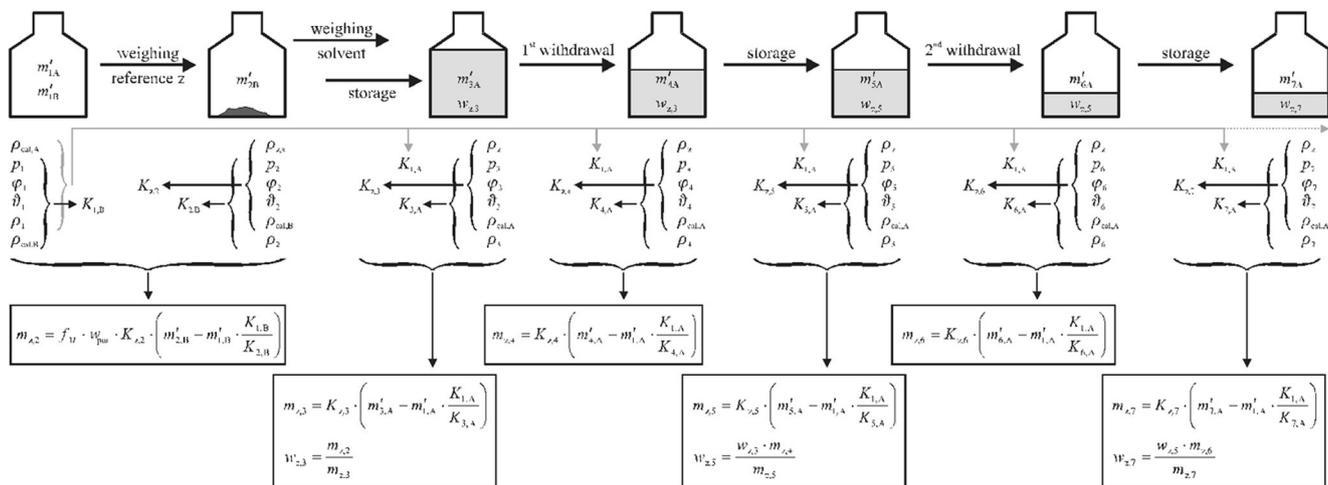

Fig. 1 Weighing scheme used to correct the mass fraction w of the analyte element in a primary elemental solution for losses due to evaporation during storage by applying the appropriate air buoyancy corrections

Next, the appropriate amount of Mo was placed in the bottle and the latter was weighed again on balance B at a time (2). This yielded the actual mass $m_{z,2}$ of Mo (since pure metallic Mo with a purity of w_{pur} was used, the stoichiometric factor, f_M, becomes 1). For more details, refer to Fig. 1:

$$m_{z,2} = f_M \times w_{pur} \times K_{z,2} \times \left(m'_{2,B} - m'_{1,B} \times \frac{K_{1,B}}{K_{2,B}} \right) \qquad (4)$$

Subsequently, the Mo was dissolved (see above) and the solution was adjusted to yield the intended Mo mass fraction by adding the appropriate amount of solvent. Before withdrawing a sub-sample from the bottle at a time (3), the bottle was weighed again on balance A to be able to calculate the recent mass fraction $w_{z,3}$ of Mo corrected for evaporation losses:

$$m_{z,3} = K_{z,3} \times \left(m'_{3,A} - m'_{1,A} \times \frac{K_{1,A}}{K_{3,A}} \right) \qquad (5)$$

$$w_{z,3} = \frac{m_{z,2}}{m_{z,3}} \qquad (6)$$

To enable the calculation of future mass fractions after the next storage time(s), the bottle was also weighed after the first withdrawal to determine the amount of Mo (solution) remaining in the bottle:

$$m_{z,4} = K_{z,4} \times \left(m'_{4,A} - m'_{1,A} \times \frac{K_{1,A}}{K_{4,A}} \right) \qquad (7)$$

These alternating storage periods and withdrawals can be described in general:

i^{th}	weighing with	i	$\in$	$N^* \backslash \{1,2\}$	$=$	$\{3,4,5,...\}$
k^{th}	withdrawal with	k	$\in$	N^*	$=$	$\{1,2,3,...\}$
	and $w_{z,i}$ with	i	$=$	$2 \times k + 1$	$=$	$\{3,5,7,...\}$

$$m_{z,i} = K_{z,i} \times \left(m'_{i,A} - m'_{1,A} \times \frac{K_{1,A}}{K_{i,A}} \right) \qquad (8)$$

$$w_{z,i} = \frac{w_{z,i-2} \times m_{z,i-1}}{m_{z,i}} \qquad (9)$$

The Rh mass fraction was calculated accordingly. In this work, several primary Mo and Rh solutions with SI-traceable mass fractions of $w(E) \approx 1$ g/kg (approximately 1 g/L) and an associated relative expanded uncertainty of $U_{rel}(w) \leq 0.05$ % were prepared. The uncertainties according to the *Guide to the Expression of Uncertainty in Measurement* (GUM) [19] were calculated using the software GUM Workbench Pro 2.4.1.392 (Metrodata GmbH, Germany) considering [20].

Measurement method To be able to compare two Mo or Rh solutions with each other (e.g., to link a secondary or transfer standard to the primary solution) on the highest metrological level (best precision and accuracy), a standard bracketing procedure with an IS was developed and implemented successfully using an ICP OES as well as an MC-ICP-MS.

Two blends (1) and (2) of a well-known standard solution (z) of the analyte element having an analyte mass fraction w_z with the internal standard solution (y) and one blend (bx) of an unknown sample solution (x) with the same internal standard solution (y) were prepared (Fig. 2). Suitable masses m of the solutions were mixed to yield an intensity ratio close to unity in the sample blend (bx) (in order to minimize biases due to detector dead time, CCD readout rates, etc.) and intensity ratios in the standard blends (1) and (2) of ± 5 % around this unity ratio (bracket). The mass fraction w_x of the analyte in the sample was calculated according to Eq. (10). This equation is derived in the Appendix. R denotes the intensity ratio of the internal standard Y over the analyte element E.

$$w_x = w_z \times \frac{m_{yx}}{m_x} \times \frac{R_1 - R_2}{\frac{m_{y1}}{m_{z1}} \times (R_{bx} - R_2) + \frac{m_{y2}}{m_{z2}} \times (R_1 - R_{bx})} \qquad (10)$$

Since it was not the intention to determine absolute analyte mass fractions but to determine how accurate and precise two
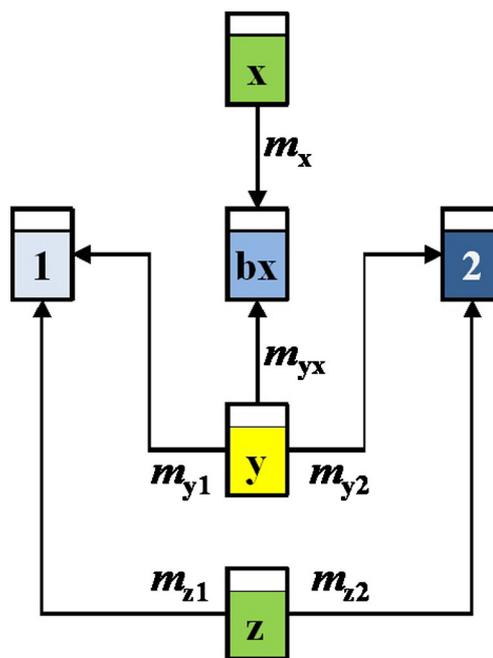
Fig. 2 Preparation of the blends (1), (2), and (bx) for the bracketing measurements with one unknown sample (x) as an example. The internal standard (y) is added at the "same" time to this sample and to two aliquots of a well-known standard solution (z). The preparation is adjusted to ensure that the standard blends (1) and (2) always form a bracket intensity ratio-wise around the sample blend (bx), aiming at intensity ratios of ± 5 % with a sample blend ratio close to unity

(primary) solutions can be compared to each other, all three blends (bx), (1), and (2), were prepared from the same primary solution. The resulting mass fraction was then compared to the one calculated from the gravimetric preparation. In a second step, one primary solution was used to prepare the blends (1) and (2), while the sample blend (bx) was prepared from another primary solution. This way the uncertainty associated with the comparison of two (primary) solutions was estimated.

Bracketing measurements with inductively coupled plasma optical emission spectrometry All measurements were performed using a commercial Spectro Ciros CCD (SPECTRO Analytical Instruments GmbH, Germany). Table 1 summarizes the main instrumental settings. Yttrium served as the internal standard in the case of both the Mo and the Rh measurements.

Within a 3-h sequence the sample blend (bx) and the blends (1) and (2) were measured in turn, starting and ending with blend (1), see Fig. 3. Twenty measurements of blend (bx) were bracketed with 11 measurements of blend (1) and ten of blend (2). To compare different solutions, one primary solution was used to prepare blends (1) and (2), while blend (bx) was prepared from a second primary solution. The relative expanded uncertainty U_{rel} according to [19] associated with the comparison of the two primary solutions ranged between 0.1 % (Mo) and 0.2 % (Rh). The uncertainty calculations were carried out with the software GUM Workbench Pro.

Bracketing measurements with multi-collector inductively coupled plasma mass spectrometry All measurements were performed using a commercial ThermoFisher Scientific Neptune double-focusing MC-ICP-MS equipped with 9 Faraday detectors coupled to 10^{11} Ω resistors. The mass spectrometer is equipped with an additional air laminar flow filter system (Spetec Laminar Flow Box FBS-V 75, class H14, efficiency $\geq$99.995 %) for the sample introduction area. It is located in a clean and air-conditioned laboratory ($\Delta\vartheta=\pm1$ °C) accessible through an air lock. Table 2 summarizes the main instrumental settings.

Standard nickel cones and 20-mL PFA sample vials (both AHF analysentechnik, Germany) were used. Blanks were determined after an appropriate wash time and before every single measurement; they were subtracted from the subsequent measurement data accordingly.

Indium (In) served as the internal standard for the rhodium measurements. Therefore, the ^{103}Rh and ^{115}In beams were focused into two suitable Faraday cups (called L3 and H3). The measurements were performed without any changes of the magnetic and electrostatic field or acceleration voltage (so-called static mode).

In the case of molybdenum, yttrium was used as the internal standard. The ^{89}Y and ^{98}Mo beams were focused into another 2 Faraday cups (called L4 and H4). Again, the measurements were performed in static mode.

Using Eq. (10), relative expanded measurement uncertainties for the comparison of two Mo and two Rh solutions of $U_{rel}\leq$0.1 %, respectively, were obtained.

Table 1 Instrumental settings of the ICP OES, Spectro Ciros CCD

| Parameter	Setting	
Aspiration mode	Pumped	
Nebulizer	Crossflow (Spectro): 2 mL/min	
Spray chamber	Scott (Spectro)	
Cool gas flow rate	13 L/min	
Auxiliary gas flow rate	1.2 L/min	
Sample gas flow rate	0.85 L/min	
RF power	1400 W	
Total measurement time	180 min	
Take-up time	90 s	
	Mo	Rh
Analyte matrix	H_2O	w(HCl)=0.01 g/g
Integration time in milliseconds	100	1000
Single measurement time in seconds	30	30
Wavelength λ in nanometers	291.192 (Mo)	343.489 (Rh)
	361.105 (Y)	324.228 (Y)
Mass fractions in blends in micrograms per gram	20 (Mo)	4 (Rh)
	1.8 (Y)	0.12 (Y)
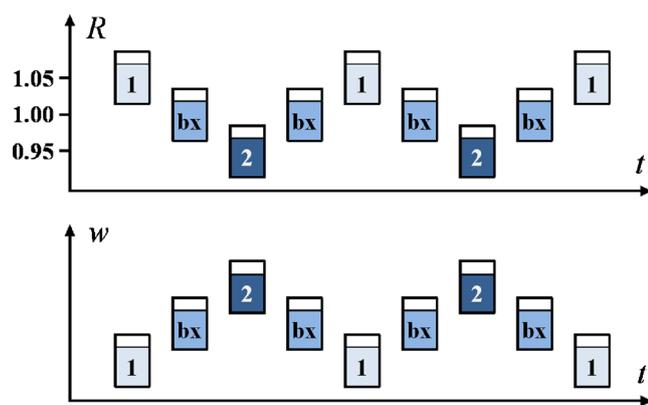
Fig. 3 Representative section of an ICP OES measurement sequence. The *upper plot* shows the intensity ratio *R* of the internal standard yttrium over the analyte element, molybdenum, or rhodium, on the *y*-axis and the measurement period *t* on the *x*-axis. The *lower plot* displays the corresponding mass fraction *w* of the element of interest (Mo or Rh) over the measurement period *t*. Both blends (1) and (2) contain the same amount of the internal standard (yttrium), but blend (1) contains a 5 % lower amount of the analyte element and blend (2) a 5 % higher amount of the analyte element compared to the mass fraction in the sample blend (bx)

Results and discussion

Three primary Mo stock solutions with w(Mo)≈4 g/kg and three primary Rh stock solutions with w(Rh)≈1.5 g/kg as well as several primary solutions with w(E)≈1 g/kg were prepared according to the highest metrological standards to yield relative expanded measurement uncertainties associated with gravimetrically determined mass fractions w of $U_{rel}(w) \leq 0.05$ %. These uncertainties include the purities of the solid starting materials as well as all contributions due to preparation and storage. The purity of the starting materials is by far the largest contribution to the uncertainties, with a relative contribution close to 99 % and, hence, also the limiting contribution to the uncertainties associated with the mass fractions of the primary solutions (Fig. 4a). The weighing of the solid materials increases the total uncertainties only slightly (less than 1 %). The uncertainties associated with handling, storage, and air buoyancy can be neglected in practice, at least at the very beginning of the lifetime of such a solution. After a certain storage period, these uncertainties become more and more important.

The bracketing plus internal standard-based measurement procedures intended to be used to compare the primary solutions with each other and to relate the primary solutions to

Table 2 Instrumental settings of the MC-ICP-MS, ThermoFisher Scientific Neptune

| Parameter	Setting	
Instrument	MC-ICP-MS (ThermoFisher Scientific Neptune)	
Autosampler	ESI-SC-Micro Autosampler	
Aspiration mode	Self-aspirating	
Nebulizer	PFA nebulizer: 150 µL/min	
Wash time	5 min	
Take-up time	45 s	
Spray chamber	Combined cyclonic and Scott (quartz)	
Cones	Sampler and skimmer (H) made of nickel	
Cool gas flow rate	16 L/min	
Auxiliary gas flow rate	0.75 L/min	
Sample gas flow rate	1.00–1.11 L/min	
Guard electrode	On	
RF power	1200 W	
Mass resolution mode	Low resolution ($M/\Delta M \approx 300$)	
	Mo	Rh
Analyte matrix	H_2O	w(HCl)=0.01 g/g
Integration time in seconds	2	4
Number of blocks per analysis	42	60
Blocks per cycle	1	1
Single measurement time in seconds	425	731
Total measurement time in hours	11	12
Sensitivity in volts/(micrograms per gram)	4 (^{98}Mo)	45
Mass fractions in nanograms per gram	1250 (Mo)	225 (Rh)
	290 (Y)	185 (In)
Long-term precision	≤0.1 %	≤0.1 %
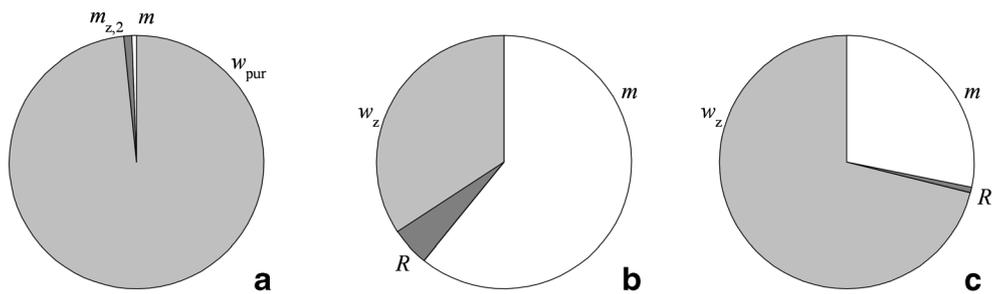
Fig. 4 Preparation and measurement of a Mo solution, **a** uncertainty contributions for the gravimetrically prepared solution containing $w(E)=$ 1 g/kg. The *pie chart* shows that 98.5 % of the uncertainty results from the impurity of the solid starting material (w_{pur}). The mass of the solid material ($m_{z,2}$) has only a contribution of less than 1 % and a negligible part is associated with handling, storage, and air buoyancy during preparation and dilution (m); **b** the result of a typical ICP OES measurement is dominated by three main contributions: masses (m) during preparation of the blends (61 %), mass fraction (w_z) of molybdenum or rhodium in the standard solution used to prepare the blends (1) and (2) (34 %), and the measurement of the signal intensity ratios (R) (5 %); **c** in the case of a typical MC-ICP-MS measurement, the same contributions add up to nearly 100 %, but with different abundances, m with 28 %, w_z with 71 %, and R with less than 1 %

transfer or commercial solutions in order to establish metrological traceability of the commercial solution showed fit-for-purpose measurement uncertainties of $U_{rel} \leq 0.2$ % (ICP OES) and $U_{rel} \leq 0.1$ % (MC-ICP-MS). A comparison between the measurement results obtained by ICP OES and MC-ICP-MS shows that both measuring techniques are suitable to recover the mass fraction calculated from the gravimetric preparation (Fig. 5): for example, all results for the Mo solution (internally called Mo-1-15.1) are consistent within the limits of uncertainty. Naturally, the uncertainty associated with the Mo mass fraction calculated from the preparation ($U_{rel}=0.05$ %) is the limiting uncertainty because this mass fraction is an input quantity of the measured Mo mass fractions. While the MC-ICP-MS measurement adds only a small amount to this uncertainty, resulting in an uncertainty associated with the measured Mo mass fraction of $U_{rel}=0.061$ %, the ICP OES measurement

adds a little more, so that uncertainties of $U_{rel}=0.10$ % were obtained. When looking at the different distributions of the main contributions to the uncertainties associated with measured Mo mass fractions (Fig. 4b, c), it becomes obvious that in the case of the MC-ICP-MS, the mass fraction of the primary solution used to prepare the calibration blends (1) and (2) is by far the largest contribution, even though the absolute uncertainty of this mass fraction is equal in both cases. The reason for this is the uncertainty associated with the intensity ratios, which is nearly 1 order of magnitude better (smaller) in the case of the MC-ICP-MS compared with the ICP OES. Another reason (which could open up the possibility for future improvements) is the much higher sensitivity of the MC-ICP-MS necessitating one more dilution step on the way to the preparation of the blends (1), (2), and (bx), resulting in larger masses with a smaller relative uncertainty. This finding means in turn that

Fig. 5 Measurement results obtained with an ICP OES and an MC-ICP-MS compared to the reference value calculated from the gravimetric preparation of a Mo solution. Within their limits of uncertainty all results are consistent with each other. The uncertainty obtained with the MC-ICP-MS ($U_{rel}=0.061$ %) is approximately 30 % smaller than that obtained with the ICP OES ($U_{rel}=0.10$ %), while the uncertainty associated with the preparation is $U_{rel}=0.05$ %
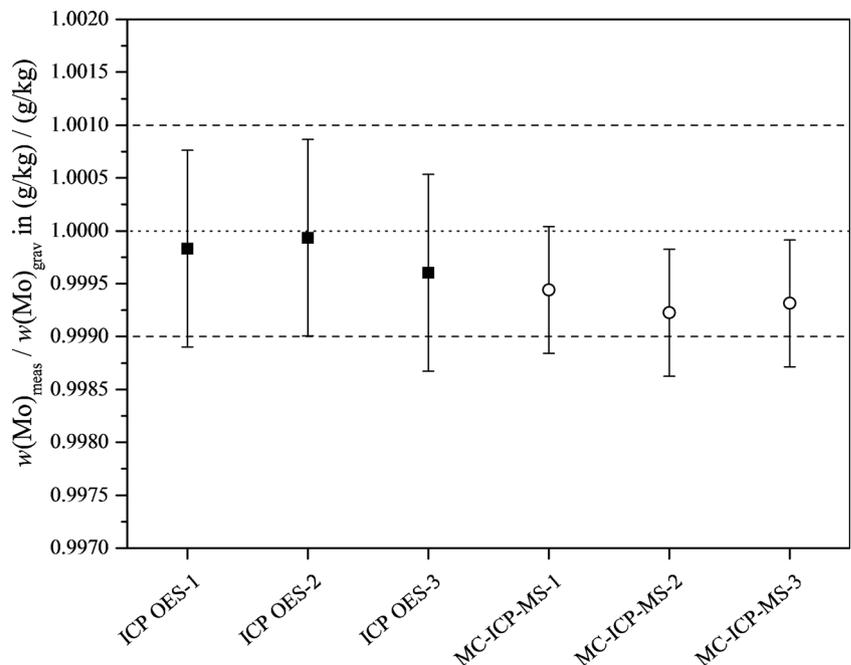
(because the Mo mass fraction w_z is the limiting contribution and both the measurement itself and the preparation do not add that much) the MC-ICP-MS measurement procedure is capable of comparing two or more solutions to each other without limits caused by the measurement. Therefore, this method was applied for the validation of the dissolution procedure: several diluted primary solutions (w(E)≈1 g/kg), prepared from different stock solutions, were measured against each other. The measured mass fractions were in agreement with the values calculated from the gravimetric preparation, validating the preparation procedure via the measurement procedure and vice versa. Hence, the basis for the preparation of commercial Mo and Rh 1 g/kg solutions with a conservatively estimated actual expanded uncertainty of $U_{rel}(w)\leq 0.5$ % has been established.

Appendix

Bracketing plus internal standard method

In the case of a linear relationship of the measured signal intensity I of an element E or isotope I and the amount of substance n of this element or isotope carried into the measurement device (e.g., ICP OES), a straight line connecting the two standard solutions (bracket) can be assumed. Its parameters slope $\tan\alpha$ and y-intercept R_0 can then be applied to calculate the mass fraction w_x of the element in the original sample. If all solutions were additionally doped with an internal standard Y, having a mass fraction of w_y, the straight line can be expressed via signal intensity and amount of substance ratios, respectively (Fig. 6).
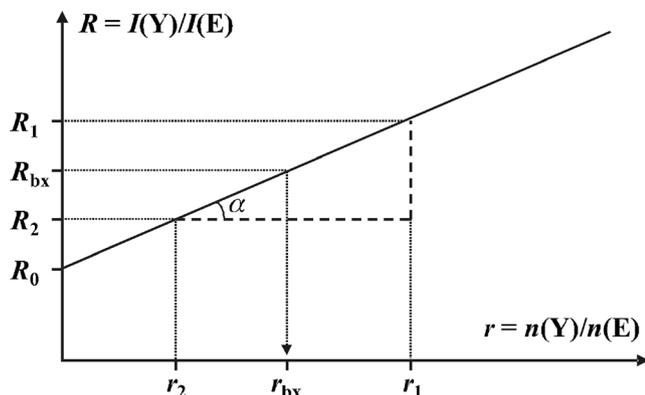

Fig. 6 Relationship between signal intensity ratios R and amount of substance ratios r used to derive Eq. (10) for the calculation of the mass fraction of the analyte element in the original sample (x)

$$r_{bx} = \frac{n_{bx}(Y)}{n_{bx}(E)} = \frac{M_x(E) \times w_y \times m_{yx}}{M(Y) \times w_x \times m_x}$$

$$r_1 = \frac{n_1(Y)}{n_1(E)} = \frac{M_z(E) \times w_y \times m_{y1}}{M(Y) \times w_z \times m_{z1}}$$

$$r_2 = \frac{n_2(Y)}{n_2(E)} = \frac{M_z(E) \times w_y \times m_{y2}}{M(Y) \times w_z \times m_{z2}}$$

$$R_{bx} = \frac{I_{bx}(Y)}{I_{bx}(E)}, \quad R_1 = \frac{I_1(Y)}{I_1(E)}, \quad R_2 = \frac{I_2(Y)}{I_2(E)}$$

$$\tan\alpha = \frac{R_1 - R_2}{r_1 - r_2}$$

$$R_0 = R_2 - (r_2 - 0) \times \frac{R_1 - R_2}{r_1 - r_2}$$

$$R_{bx} = R_0 + (\tan\alpha) \times r_{bx}$$

$$r_{bx} = \frac{R_{bx} - R_0}{\tan\alpha} = \frac{R_x - R_2 + r_2 \times \frac{R_1 - R_2}{r_1 - r_2}}{\frac{R_1 - R_2}{r_1 - r_2}}$$

$$r_{bx} = \frac{R_{bx} \times (r_1 - r_2) - R_2 \times (r_1 - r_2) + r_2 \times (R_1 - R_2)}{R_1 - R_2}$$

$$r_{bx} = \frac{R_{bx} \times r_1 - R_{bx} \times r_2 - R_2 \times r_1 + R_2 \times r_2 + r_2 \times R_1 - r_2 \times R_2}{R_1 - R_2}$$

$$r_{bx} = \frac{r_1 \times (R_{bx} - R_2) + r_2 \times (R_1 - R_{bx})}{R_1 - R_2}$$

$$\frac{M_x(E) \times w_y \times m_{yx}}{M(Y) \times w_x \times m_x} = \frac{M_z(E) \times w_y}{M(Y) \times w_z} \times \frac{\frac{m_{y1}}{m_{z1}} \times (R_{bx} - R_2) + \frac{m_{y2}}{m_{z2}} \times (R_1 - R_{bx})}{R_1 - R_2}$$

$$w_x = w_z \times \frac{M_x(E)}{M_z(E)} \times \frac{m_{yx}}{m_x} \times \frac{R_1 - R_2}{\frac{m_{y1}}{m_{z1}} \times (R_{bx} - R_2) + \frac{m_{y2}}{m_{z2}} \times (R_1 - R_{bx})}$$

In case the isotopic composition of the element of interest is the same in the sample and in the standard, the ratio of the molar masses cancels from the last equation.

$$w_x = w_z \times \frac{m_{yx}}{m_x} \times \frac{R_1 - R_2}{\frac{m_{y1}}{m_{z1}} \times (R_{bx} - R_2) + \frac{m_{y2}}{m_{z2}} \times (R_1 - R_{bx})}$$

In case a mass spectrometer is used and the element of interest has at least two isotopes, the amount of substance fractions x of the isotope of the analyte element measured in sample x and in standard z have to be taken into account.

$$w_x = w_z \times \frac{x_z(I)}{x_x(I)} \times \frac{M_x(E)}{M_z(E)} \times \frac{m_{yx}}{m_x}$$

$$\times \frac{R_1 - R_2}{\frac{m_{y1}}{m_{z1}} \times (R_{bx} - R_2) + \frac{m_{y2}}{m_{z2}} \times (R_1 - R_{bx})}$$

Quantities, indices, and other symbols

Table 3 summarizes all quantities, indices, and additional symbols used throughout the document.

Table 3 List of all symbols

Quantities		
Symbol	Unit	Definition
m	g	Mass
m'	g	Weight (balance reading)
M	g/mol	Molar mass

Table 3 (continued)

Quantities

Symbol	Unit	Definition
w	g/g	Mass fraction
ρ	kg/m^3	Mass density
p	hPa	Air pressure
ϑ	°C	Air temperature
φ	1	Relative humidity of the air
K	g/g	Air buoyancy correction factor
w_{pur}	g/g	Purity of the solid material (metal or salt) used to prepare the stock solution
f_M	1	Stoichiometric factor, e.g., in the case of a sodium solution prepared from sodium chloride: $f_M = M(Na)/[M(Na)+M(Cl)]$
R	1	Intensity ratio of the internal standard over the analyte element
I	V or s^{-1}	Signal intensity
r	1	Amount of substance ratio of the internal standard over the analyte element
n	mol	Amount of substance
t	s	Time or duration
U_{rel}	%	Relative expanded measurement uncertainty

Indices (gravimetric preparation scheme)

Symbol	Definition
A	Weighed on balance A (H315, Mettler Instrumente AG, Switzerland)
B	Weighed on balance B (MC210S, Sartorius AG, Germany)
1	Time 1, weighing of the empty bottle
2	Time 2, weighing of the bottle plus solid (metal or salt) material used to prepare the stock solution
3	Time 3, weighing of the bottle plus stock solution prior to the first withdrawal of an aliquot of the stock solution
4	Time 4, weighing of the bottle plus remaining stock solution after the first withdrawal of an aliquot of the stock solution
5	Time 5, weighing of the bottle plus stock solution prior to the second withdrawal of an aliquot of the stock solution
6	Time 6, weighing of the bottle plus remaining stock solution after the second withdrawal of an aliquot of the stock solution
7	Analog to 3 and 5
cal	…of the calibrated reference weight
air	…of the air

Indices (bracketing plus internal standard method)

Symbol	Definition
x	… of the sample
y	… of the internal standard
z	… of the standard (solution)
bx	… of the blend prepared from the sample and the internal standard
1	… of the blend prepared from the standard and the internal standard with an intensity ratio R slightly higher than in blend bx

Table 3 (continued)

Quantities

Symbol	Unit	Definition
2		… of the blend prepared from the standard and the internal standard with an intensity ratio R slightly lower than in blend bx

Other symbols

E	Chemical element (e.g., Rh or Mo) of interest (analyte element)
Y	Chemical element serving as the internal standard (e.g., In)
I	Isotope of a chemical element (e.g., ^{98}Mo)

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