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ICP-MS analysis of high purity molybdenum used as SI-traceable standard of high metrological quality

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The need, concept and technical approach for the certification of SI-traceable standards of high metrological quality for chemical analysis of the elements is briefly explained. As an example of problems occurring in the certification of these standards, special technical aspects related to the analysis of high purity Mo by ICP-MS, namely blank reduction for Na, Li and Ni by protective coating of the cones with silicon, as well as dealing with the interferences from the Mo matrix, are discussed.

Introduction

Instrumental methods based on atomic spectrometry are widely used for elemental analysis. For calibration, typically solutions are used, which are prepared gravimetrically from high purity materials in the laboratory or on the production line of a commercial producer. Typically the purity of the starting material is only known with respect to some metallic analytes. In most cases there is no information on non-metals (especially oxygen, but also carbon, hydrogen, halogens and others), which often cause significant impurity contributions. The example in Table 1 nicely illustrates the errors which can be made, when this partial information is taken to be synonymous with the total purity of the material.

Although the larger commercial producers of calibration solutions and the National Metrology Institutes (NIMs) especially make quite an effort to analyse these starting materials for impurities, with many elements the problem remains that usually the purity of the material is known insufficiently well.[1] Even today a programme for *fully* characterised high purity substances serving as metrological embodiment of the Système International d'Unités (SI) for chemical analysis is nationally and internationally lacking, in all cases causing concern over the comparability of data and SI-traceability. One has to admit that the size of the problem is dependent on the level of measurement uncertainty required.

At BAM a system of primary standards for element analysis is being developed to overcome this lack. The target uncertainty (according to GUM)[2] of the mass fraction of the matrix element is 0.01%. In close collaboration with Physikalisch-Technische Bundesanstalt (PTB) the materials are the National Standards for Elemental Analysis in Germany. By cooperation with other NMIs the developed system is aiming to contribute to international harmonisation. Since there is no method of measurement to achieve this target uncertainty directly, the mass fractions of the impurities are measured, summarised and subtracted from the ideal purity of 1 kg kg^{-1}. *All* elements of the periodic table not being the matrix element must considered to be impurities, which need to be measured. An example of a completely successful impurity measurement of a high purity material is BAM-A-primary-Cu-1[3–10] with a result for the purity statement of w(Cu, BAM-A-primary-Cu-1) = $(0.999\,968 \pm 0.000\,010)$ kg kg^{-1}. The wide span of impurities involved in the full characterisation of high purity materials requires huge effort and to have a variety of measurement methods and techniques available (Table 2). ICP-MS plays an important role in this work. Special technical aspects of the analysis in Mo matrix by ICP-MS are presented further as an example of problems encountered.

Special technical aspects in the analysis of high purity Mo by ICP-MS

Trace determination of the alkali elements is, in general, difficult, due to the blanks from the environment and from certain compounds of the instrument (*e.g.*, cones and torch in ICP-MS measurements). In ICP-MS measurements a reduction of the instrumental blanks can be achieved by applying the cold plasma technique as described in ref. 11. However, this is only possible on cost of a decreased robustness of the plasma.

An empirical approach to the reduction of the instrument blank is "conditioning". Rodushkin[12] reports a reduction of the instrument blanks from the sampler and skimmer cones when flushing the instrument for 10–15 min with a urine matrix (10-fold diluted urine) prior to the actual measurement. The formation of a salt crust on the cones of the ICP-MS inlet was assumed to be responsible for this effect.

In our ICP-MS rather high blanks for Li, Na and Ni, as well as memory effects for Li and Na, have been observed in the analysis of matrix free solutions (*e.g.*, high purity water for microelectronic purposes), when mounting unused Ni-cones as obtained from the manufacturer. Furthermore, in the analysis of a molybdenum matrix (1.2 g l^{-1}) the measurement of Li and Na turned out to be impossible at the low mg kg^{-1} level (related to the solid Mo), because in addition to the rather high blanks and the memory effect, a matrix depression of 30–50% relative was observed. Remembering, that in the earlier analysis of high purity Si we observed very low blanks for Na, Li and Ni, the old cones from the silicon analysis were mounted and, after applying the usual rinsing procedure, very much lower blanks for Na, Li and Ni for matrix free solutions were obtained. This led to systematic investigations on the influence of a protective coating of the cones with silicon. Finally, the protective coating was applied to improve the measurement of Li and Na in a Mo matrix. In the period of the review process, Engström *et al.*[13] reported the application of silicon coated cones for the reduction of blanks and oxide rates in the analysis of soft biological tissue.

For our application, the purity analysis of high purity substances by ICP-MS, the aim is to measure as many impurities as possible with only reasonable effort. With this in mind, the often very time consuming special techniques for matrix separation or pre-concentration of analytes are not applicable. The material is decomposed, dissolved, diluted using high purity acids and water and finally analysed at a matrix

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Table 1 Mass fraction of copper in two high purity materials: (A) nominal metallic purity as stated by the supplier, (B) metallic purity as measured and (C) total purity as measured

	BAM-B-primary-Cu-1	BAM-A-primary-Cu-1
A	0.999 999	0.9999
B	0.999 997 ± 0.000 002	0.999 978 ± 0.000 010
C	0.999 44 ± 0.000 17	0.999 969 ± 0.000 010

concentration of about 1 g l^{-1}. With this approach nearly 70 elements can be measured in different matrix solutions by ICP-MS. Using different resolution settings, the commonly known spectral interferences by polyatomic ions (*e.g.*, $^{56}Fe^+$/$^{40}Ar^{16}O^+$; $^{44}Ca^+$/$^{12}C^{16}O_2{}^+$) can be overcome, at the cost of sensitivity, however.

In the analysis of molybdenum, a couple of matrix induced spectral interferences, mainly interfering with the analytes Ba, Cd, Ce, Cs, Dy, In, Nb, Nd, Pr and Ti need to be investigated.

Experimental

For the ICP-MS measurements an Element I (Finnigan MAT) was used, applying the instrumental parameters as summarised in Table 3. Nickel cones from R. A. Chilton ICPMS Cones Ltd. (UK) have been used. A tuning solution containing Li, B, Na, Sc, Co, Zn, Y, In, Rh, Ba, Ce, Lu, Tl and U at 10 µg l^{-1} in 1% (v/v) nitric acid was used to optimise daily the instrumental parameter and to perform the mass calibration in the different resolution settings. The tuning solution was prepared from single element standard stock solutions obtained from Merck (Darmstadt, Germany). For the investigation of the protective coating of the ICP-MS cones, a multi-element standard solution of 10 µg l^{-1} in 1% (v/v) nitric acid, prepared from ICP IV (23 elements, Merck, Germany), was used. The silicon coating was produced by nebulising a Si solution of 1000 mg l^{-1} in 1% HF (v/v) for 30 min. The silicon solution was prepared by dissolving 1 g of high purity silicon (Alfa Johnson Matthey 99.999+%) in 10 ml sub-boiling distilled hydrofluoric acid and 10 ml sub-boiling distilled nitric acid and subsequent dilution with water.

Standard solutions for the investigation of the Mo-matrix, mainly for spiking Mo containing solutions, were prepared from ICP IV and VI (30 elements, Merck, Germany) and from Spectrascan-Standards Multi #12 (11 elements) and Multi #15 (17 RE elements) (Teknolab AS, Norway). In a few special cases (*e.g.*, Ca, Cd) mono-element stock solutions (Merck, Germany) were used. Standard solutions have been prepared by dilution in PFA (A-graded) flasks in a clean bench using high purity water from an ultra-pure water system Milli-Q 185 plus (Millipore, Germany) and sub-boiling distilled acids (HNO_3, HCl, HF).

Table 2 Methods of measurement used for the purity measurement of BAM-A-primary-Cu-1

Method	Application, function
Atomic absorption spectrometry with electrothermal atomisation, hydride and cold vapour technique	Metals, Supplement and confirmation
Optical emission spectrometry with inductively coupled plasma excitation; instrumental neutron activation analysis	Metals, Supplement
Carrier gas hot extraction; photon activation analysis; noble gas mass spectrometry; activation with ^{15}N	Non metals, noble gases
High resolution mass spectrometry with inductively coupled plasma ionisation	Metals
Laser ablation with ICP-MS	Check of decomposition step
ICP-MS after flow injection	Lowering LODs
Photometry	S, F, P

Table 3 ICP-MS operating conditions and instrumental parameter

Nominal mass resolution ($m/\Delta m$)	300, 3000, 7500
Guard electrode	Not mounted
RF power	1275 W
Nebuliser	MicroFlow PFA-ST (self-aspirating)
Spray chamber	Scott type (double pass) PFA, water cooled to 5 °C
Torch	Quartz with sapphire injector (1.8 mm id)
Coolant argon flow rate	15 l min^{-1}
Intermediate argon flow rate	1.0 l min^{-1}
Nebuliser argon flow rate	1.300 l min^{-1}
Make up argon flow rate	0.300 l min^{-1}
Sample uptake rate	0.1 ml min^{-1}
Ion lens settings	Adjusted to obtain best compromise for signal intensity for isotopes in low, medium and high mass range, good peak shape and best resolution
Sampler cone	Nickel, 1.1 mm orifice diameter
Skimmer cone	Nickel, 0.8 mm orifice diameter
Acquisition mode	E-scan (in all resolution settings)
Measurement parameter (LR)	
Number of scans	3–15 (depending on analytical task)
Acquisition window	120%
Search window	100%
Integration window	80%
No. of acquisition points per nuclide	20
Dwell time per acquisition point	10 ms (up to 50 ms in HR)

Compact molybdenum from Alfa Johnson Matthey 99.97% in the form of rods with a diameter of about 3.2 mm was used. Prior to the dissolution, the molybdenum was etched for 10 s at room temperature in 4 + 1 (v/v) HF + HNO_3, and after flushing with water for 20 s at room temperature in HCl in an ultrasonic bath. After flushing with water (five times) and ethanol (three times) with the aid of an ultrasonic bath for 1 min each, the material was dried in an air flow in a clean bench. In four parallel sessions, about 0.6 g of Mo was dissolved using 5 ml HNO_3 and 1 ml HF of sub-boiling distilled acids in pre-cleaned 50 ml PFA flasks. After a reaction time of 10 min the samples were dissolved and the solutions were further heated for about 1 h at 80 °C in a water bath, cooled to room temperature and finally filled-up to the marked volume with high purity water. Blanks have been processed through the same procedure. For the measurements with ICP-MS, sample and blank were 10 fold diluted using high purity water.

For environmental scanning electron microscopy (ESEM) an ESEM XL 30 (FEI company, Oregon) was used. Raman spectra have been obtained using a DILOR-XY-Raman spectrometer.

Results and discussion

Protective coating with silicon

When rinsing the instrument equipped with new Ni cones and after the usual tuning procedure with pure water, blank intensities for Li and Na drop by a factor of about 30 within the first 13 h to reach a still high but stable level. For Ni the raw

Table 4 Background equivalent concentrations (BEC) for high purity water for Si-coated and uncoated cones

	BEC (Li)/μg l^{-1}	BEC (Na)/μg l^{-1}	BEC (Ni)/μg l^{-1}
Uncoated, before rinsing with water	8.7	7.0	1.8
Uncoated, after rinsing with water	0.210	0.200	1.6
Just after coating	0.0009	0.005	0.018
Si coated, matrix free measurements	0.0061	0.004	0.130
Si coated, after applying Mo matrix	0.011	0.038	0.230

signal remains constant at high level. When introducing a standard solution for Li, Na and Ni with a concentration of 10 μg l^{-1} each, the background equivalent concentration (BEC) for pure water at the end of the rinsing procedure can be estimated for Li, Na and Ni to be 0.21 μg l^{-1}, 0.20 μg l^{-1} and 1.6 μg l^{-1}, respectively (see Table 4). Measuring a rinse blank after the standard reveals for Li a very strong, for Na a strong and for Ni no memory effect. After coating of the cones with silicon, the background from Li, Na and Ni has been reduced by 2–3 orders of magnitude (see Table 4), while sensitivity remains nearly the same. To prove that the effect of a reduced background for Li, Na and Ni is really due to the coating of the cones and not due to a cleaning effect of the nebuliser system including rinsing with the Si solution, in later measurements silicon coated cones were installed to replace normal cones. A drastically reduced background was immediately observed for Li, Na and Ni. Rinsing again with water, the background signal suggests that rather stable measurement conditions without severe memory effects might be achievable for Li, Na and Ni. To verify this, memory effects and the stability of the blanks with and without matrix must be investigated for the coated cones.

The signal intensities for the analytes from a standard (corrected for acid blank) are alternated with the signal intensity of high purity water. A rinsing step with 1% nitric acid before and after the standard was performed. The instrument has been cleaned by rinsing with 1% (v/v) nitric acid and high purity water before the measurement. Whereas acid rinsing is known to be essential for some elements such as Bi, it was found not to be relevant for Li, Na and Ni. The background impurities for Li and Na at the beginning of this measurement series were nearly the same as compared with the background impurities after coating of the cones and slightly higher for Ni (about 5-fold). In the first measurement cycle a memory effect for Li was observed corresponding to an increase of the BEC by a factor of 10. After the first cycle, stable measurement conditions for Li, Na and Ni could be achieved for a long period of time (about 5 h) for matrix free measurements.

Figs. 1 and 2 show the signal intensity when, additionally, a matrix load of 1.2 g l^{-1} Mo is applied. The effect of rinsing with nitric acid before and after the element standard is not displayed. Also, the signals from the acid adapted blank solution for the Mo sample applied directly after the Mo sample are not displayed. In the first measurement cycle a big increase of the signal from water is observed for Na ($\approx$50-fold) and Li ($\approx$ 10-fold), whereas the signal of Ni remains about constant. After this first cycle additional water samples have been run before the matrix solution in order to distinguish between a rinsing effect of the matrix and matrix blank solution and an effect from the standard. As a consequence, the time regime has changed and the data from the first cycle is not fully compatible with the data of the others.

For Ni (Fig. 1) the background behaviour of the system seems to be stable, no memory or rinsing effect could be detected. For Li (not displayed) there seems to be a strong rinsing effect after Mo matrix has been applied to the instrument, as can be observed from the signal intensities for Li in water before and after the matrix solution, which show a difference of about half an order of magnitude. For Na (Fig. 2) a similar pattern is observed. The signal intensity for Na in water increases by about half an order of magnitude from before to after the Mo sample. The signal intensity of the Mo blank (not displayed) is about the same as the signal intensity of the Mo solution.

Since the rinsing and memory effect are time dependent, a strict rinsing regime has to be applied. The BEC for Li, Na and Ni in pure water at the end of the measurement cycles containing a matrix solution of 1.2 g l^{-1} Mo is calculated to be

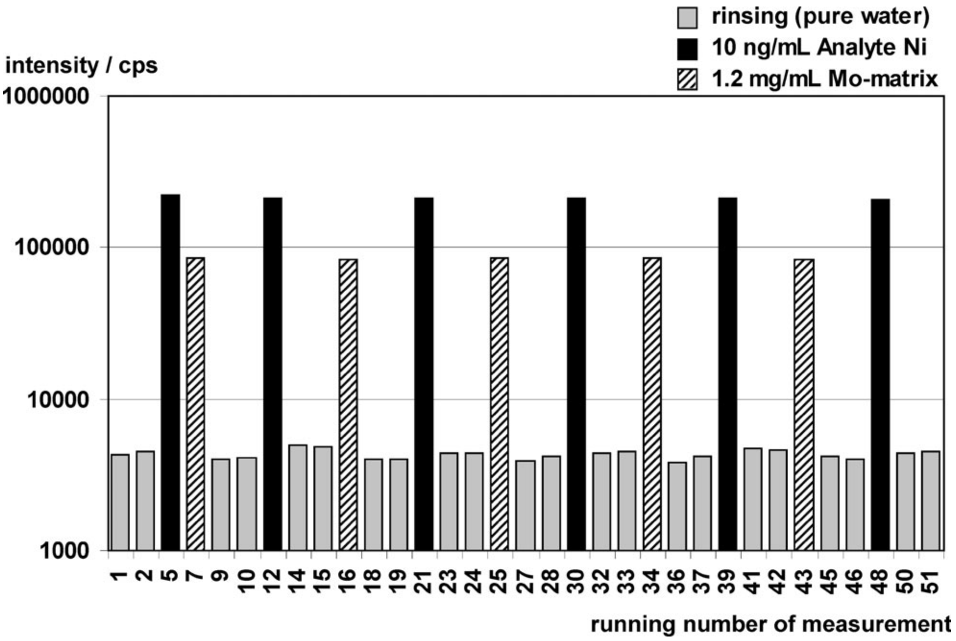

Fig. 1 Influence of 1200 mg l^{-1} Mo matrix on stability of background for Ni using silicon protected cones.

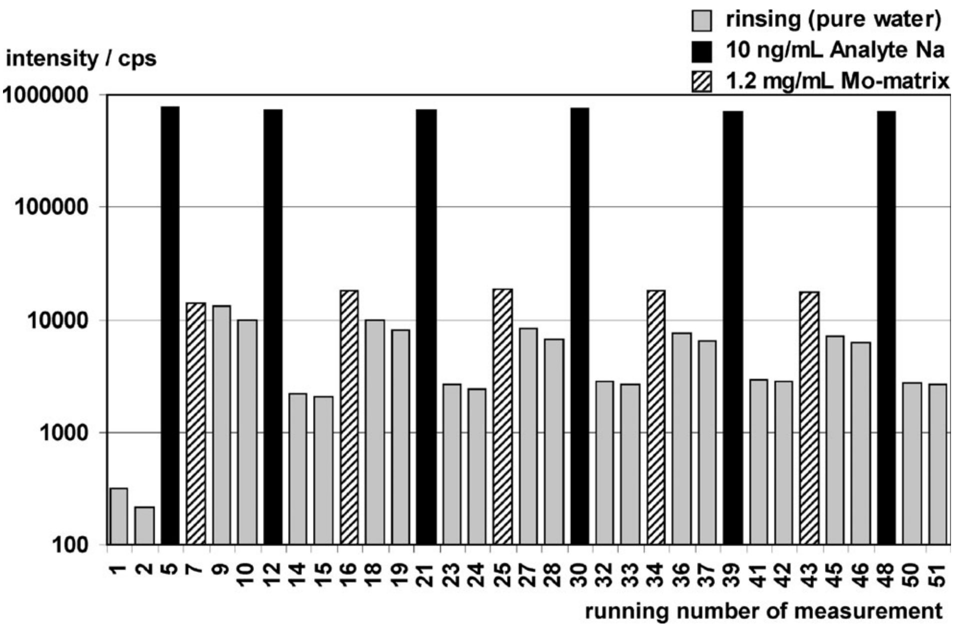

Fig. 2 Influence of 1200 mg l^{-1} Mo matrix on stability of background for Na using silicon protected cones.

0.011 µg l^{-1} for Li, 0.038 µg l^{-1} for Na and 0.23 µg l^{-1} for Ni. Even if not as good as for the matrix free analysis, the coating of the cones with silicon leads to a reduced background and reduced memory effects, thereby enabling the measurement of Li and Na at low µg g^{-1} level in solid molybdenum, which was impossible with uncoated cones. For the measurement of Ni in molybdenum an improvement was achieved. The values for the BEC obtained in the different measurement scenarios are summarised in Table 4.

Although the application of Si coated cones looks promising, a general use of this technique cannot be recommended especially for matrix containing solutions. This is because from the silicon coating additional species of polyatomic Si-containing ions (*e.g.*, SiO^+, $SiOH^+$, $SiO_2{}^+$, SiO_2H^+ and $SiAr^+$) are formed, which cause additional interferences for the elements Sc, Co and Ni as well as for particular isotopes of Cu, Zn and Ga. Conversely, for matrix free solutions most of the silicon based interferences can be resolved using medium resolution: this does not necessarily hold for matrix containing solutions, where the interference pattern gets more complex. This limits the use of silicon coated cones to special analyte/matrix combinations, as demonstrated here for the case of Li, Na and Ni in Mo.

Fig. 3 shows the ESEM pictures of the coated sampler cone: the picture of the coating on the skimmer cone is similar. The coatings seem to consist of a compact layer from spherical objects with a diameter of about 5 µm and below. The X-ray spectrum (not displayed) shows as expected only signals from nickel for the uncoated cones and only signals from silicon and oxygen for the coated cones. The Raman spectra in Fig. 4, where the spectra of quartz glass and crystalline quartz are compared with the spectrum obtained from the coating, indicates that the protective coating on the cones consists of an amorphous quartz glass.

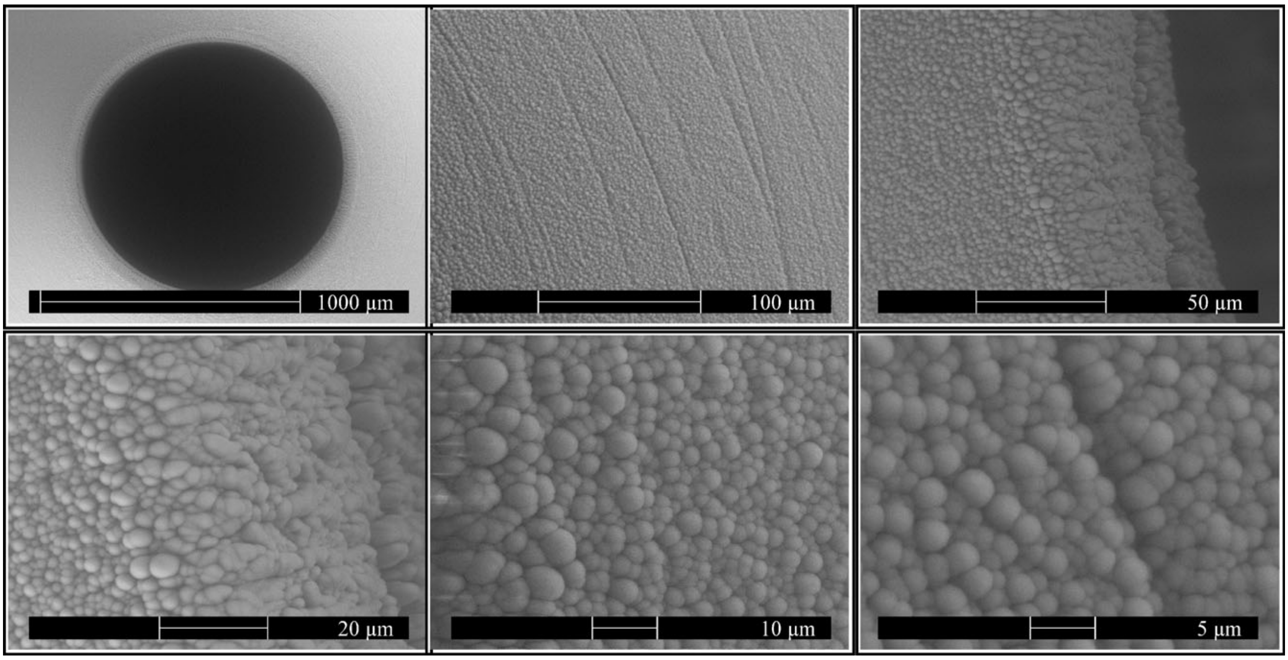

Fig. 3 ESEM pictures of the sampler cone of ICP-MS with protective coating (30 min Si 1000 mg l^{-1}).

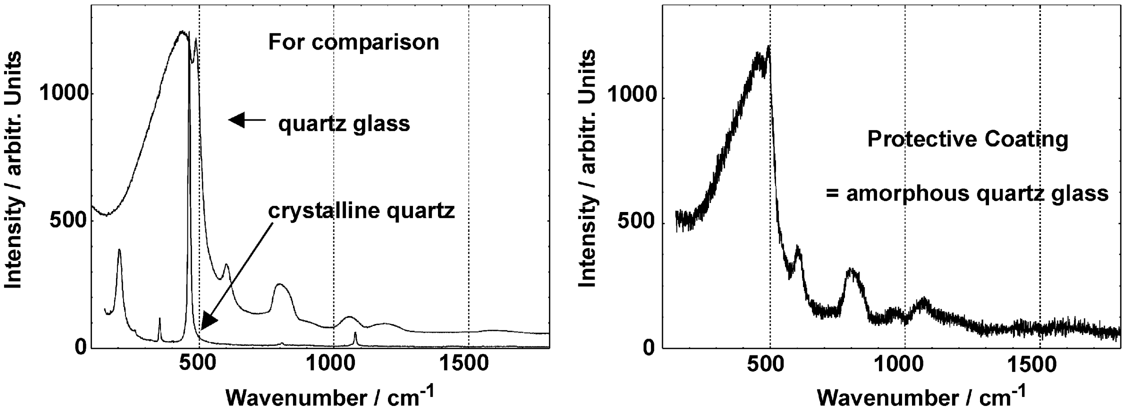

Fig. 4 Raman spectrum of protective coating on ICP-MS cones (30 min Si 1200 mg l^{-1}) compared with spectra of crystalline quartz and amorphous quartz glass.

Dealing with interferences of Mo matrix

Fig. 5 shows the mass spectrum of molybdenum (1.2 g l^{-1}) in low resolution ($m/\Delta m$ = 300) for those regions where spectral interferences from Mo could be observed. The spectral interferences could be identified as Mo containing polyatomic ion species with hydrogen, oxygen, nitrogen and argon, as well as doubly charged ions of Mo, as schematically indicated in Fig. 5. The measurement of Ba, Cd, Ce, Cs, Dy, In, Nb, Nd, Pr and Ti is disturbed by these spectral interferences. Table 5 summarises for these elements the optimal isotope for measurement, the major disturbing polyatomic ions and the mass resolution required to separate both. The interfered analytes can be separated in three groups. For the first group of elements (*i.e.*, Ba and Dy) the high resolution mode ($m/\Delta m \approx$ 7500) of the instrument is sufficient to resolve the interference. Although, for the second group of elements (*i.e.*, Ce, Nd and Ti) the signals cannot be fully resolved from the matrix interferences, a quantification is possible *via* the graphical evaluation of the peak profile. In these cases the analyte peak is visible close to the larger interfering peak, as exemplified in Fig. 6 for Ti. Using this approach limits of detection (LODs, based on 9 s) of 1 µg g^{-1} or lower can be obtained for Ce, Nd and Ti in (solid) Mo. For the last group of analytes (*i.e.*, Cd, Cs, In, Nb and Pr) the required resolution is higher than the resolution achievable with our set-up. In some cases of spectral interferences in this group, a mathematical interference correction (MIC) or a measurement in medium resolution, as in the case of Nb, can be applied to reduce the influence of the interference: however, the LOD for these analytes in solid Mo remain between 0.5 and 75 µg g^{-1}.

Measurement results for Mo

The results for the analysis of molybdenum by ICP-MS for 67 impurities are summarised in Table 6. Tungsten is the dominating impurity with a mass fraction of *w*(W, Mo) = 211 µg g^{-1}and a standard uncertainty of 11 µg g^{-1}, followed by the value for

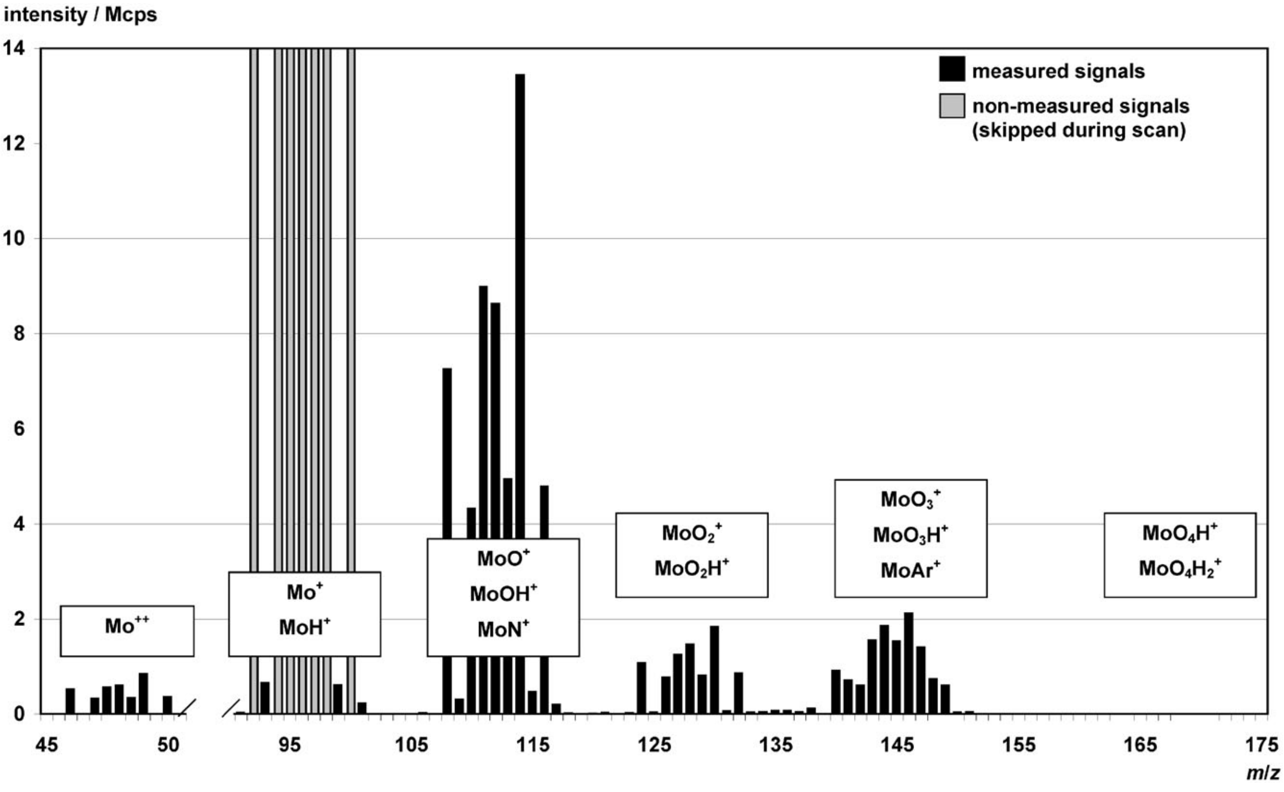

Fig. 5 Mass spectrum of peak averaged results as bar graph for molybdenum.

Table 5 Matrix interfered elements in Mo matrix (1.2 g l^{-1})

Element	Optimum isotope	Main Mo-interference	Required resolution	w_{Eq}/μg g^{-1}[b]	Resolution used	LOD in Mo/μg g^{-1}
Ba	^{138}Ba	$^{98}Mo^{40}Ar^+$	3681	1.2	HR	0.02
Dy	^{163}Dy	$^{98}Mo^{16}O_4H^+$	4542	0.1	HR	0.04
		$^{97}Mo^{16}O_4H_2{}^+$	5941		HR	
Ti	^{48}Ti	$^{96}Mo^{2+}$	10 923	6.5	HR (profile)	1.0
Ce	^{140}Ce	$^{100}Mo^{40}Ar^+$	3930	7.1		
		$^{92}Mo^{16}O_3{}^+$	10 064		HR (profile)	0.01
Nd	^{146}Nd	$^{98}Mo^{16}O_3{}^+$	6396			
		$^{97}Mo^{16}O_3H^+$	10 027	81.0	HR (profile)	0.2
Nb	^{93}Nb	$^{92}MoH^+$	11 249	6.1	MR[a] (MIC: *m/z* 101)	2.0
Cd	^{106}Cd	$^{92}Mo^{14}N^+$	30 967	17.2[c]	LR	75
	^{111}Cd	$^{95}Mo^{16}O^+$	32 333	690[c]	MR (MIC: *m/z* 106; 108)	50
		$^{94}Mo^{16}OH^+$	30 386			
In	^{115}In	$^{98}Mo^{16}OH^+$	26 911	4.9	MR (MIC: *m/z* 117)	5
Cs	^{133}Cs	$^{100}Mo^{16}O_2H^+$	428 726	0.3	LR	0.5
Pr	^{141}Pr	$^{92}Mo^{16}O_3H^+$	16 996	5.1	LR (MIC: *m/z* 147)	5

[a] Application of medium resolution (MR) to reduce the continuos Mo background. [b] Equivalence mass fraction estimated from sensitivity of ^{138}Ba in Mo matrix in low resolution (LR). [c] Only first approximation, because the high ionisation potential of Cd has not been accounted for.

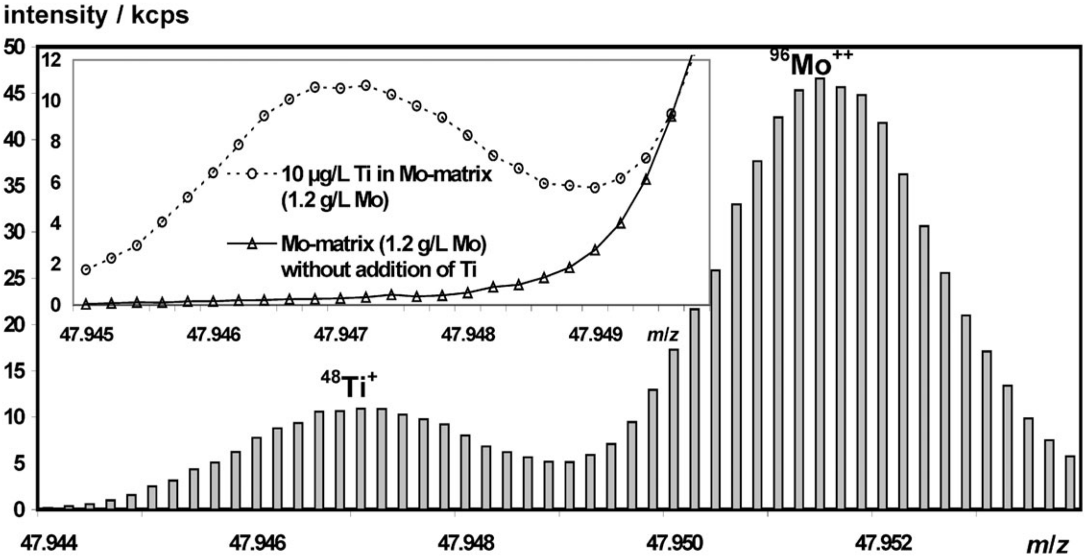

Fig. 6 ICP-MS spectrum of the interference $^{96}Mo^{2+}$ on $^{48}Ti^+$ in high resolution (HR).

cadmium with a conservative upper limit of w(Cd, Mo) $<$ 50 μg g^{-1}. Here independent methods of measurement must be used to validate the results and to reduce the upper limit value for Cd.

At first glance the Mo-material does not seem to be very suitable as material of type A, due to the rather high visible impurity content. Most likely there are Mo-materials (powder, foil) available with much lower metallic impurities. However, as explained above, the total impurity is what matters and there is no point in using a material with fewer metallic impurities but a huge surface/volume ratio introducing a large oxygen impurity or a material from a very small batch, rarely sufficient for the purity analysis. Note that a final decision on the suitability of a material can only fall after all impurities have been measured.

Conclusion

In the analysis of matrix free samples improvements in the analytical performance for Li, Na and Ni by 2–3 orders of magnitude were achieved, when coating the ICP-MS cones with silicon. For the analysis of Mo matrix still an improvement of 1–2 orders of magnitude were gained. The composition of the coating on the ICP-MS cones was found to be amorphous quartz glass.

When aiming at a broad selection of analytes, spectral interferences caused by the matrix in the purity analysis of high purity molybdenum can be overcome by high resolution measurements for Ba and Dy. For Ce, Nd and Ti a quantification can be performed down to limits of determination below 1 μg g^{-1} with respect to the solid Mo using a graphical peak profile evaluation. For the impurities with Cd, Cs, In, Nb and Pr only a worst case estimate can be made, because the interferences cannot be resolved in high resolution mode ($m/\Delta m = 7500$).

High purity substances fully characterised for impurities seem to be indispensable for the chemical measurements system. The way to establish these materials is full of challenges and problems.

Table 6 Measurement results for the analysis of Mo by ICP-MS as mass fractions w(E, Mo) (in italics) or as conservative upper limit of w(E, Mo); the standard uncertainties are estimated to be 5% relative for tungsten and 15% relative for all other elements; for Ca, Al, Mg and rare earth elements recovery and sensitivity were checked by standard addition experiments in HNO_3 and HNO_3–HF. Th is assumed to behave in the same way. n.m. = not measured; (MI) = matrix interference (not fully resolved with $m/\Delta m = 7500$)

E	w(E, Mo)/μg/g	E	w(E, Mo)/μg/g	E	w(E, Mo)/μg/g
Ag	<0.05	Ho	<0.01	Ru	<0.01
Al	*0.66*	I	n.m.	S	<25
As	*1.2*	In	<5 (MI)	Sb	*1.3*
Au	<0.02	Ir	<0.02	Sc	<0.01
B	n.m.	K	*6.9*	Se	<2
Ba	*0.11*	La	<0.005	Si	n.m.
Be	<0.5	Li	<1	Sm	<0.01
Bi	<0.05	Lu	<0.001	Sn	<0.5
Br	n.m.	Mg	<0.1	Sr	<0.01
Ca	<1	Mn	*0.92*	Ta	<0.1
Cd	<50 (MI)	Mo	Matrix	Tb	<0.001
Ce	*0.52* (MI)	Na	<2	Te	<5
Co	<0.1	Nb	<2 (MI)	Th	*0.043*
Cr	*10.6*	Nd	<0.5 (MI)	Ti	<1 (MI)
Cs	<0.5 (MI)	Ni	*5.4*	Tl	<0.01
Cu	*0.42*	Os	n.m.	Tm	<0.001
Dy	<0.05	P	*2.1*	U	<0.01
Er	<0.01	Pa	<0.005	V	*0.78*
Eu	<0.01	Pb	<0.05	W	*211*
Fe	*17.9*	Pd	<0.02	Y	<0.01
Ga	<0.1	Pr	<5 (MI)	Yb	<0.005
Gd	<0.01	Pt	<0.02	Zn	<0.2
Ge	<0.1	Rb	*0.41*	Zr	<0.1
Hf	<0.005	Re	<0.2		
Hg	<0.2	Rh	<0.01		

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References

1 J. R. Moody, R. R. Greenberg, K. W. Pratt and T. C. Rains, *Anal. Chem.*, 1988, **60**, 1206A–1218A.

2 ISO, *Guide to the expression of uncertainty in measurement*, ISO, Geneva, 1993.

3 Certificate BAM-Y001, BAM, 2004.

4 H. Kipphardt, *Certification report BAM-Y001*, BAM, 2004.

5 R. Matschat, M. Czerwensky, S. Pattberg, H.-J. Heinrich and S. Tutschku, *Mater. Trans. JIM*, 2002, **43**, 90–97.

6 H. Kipphardt, T. Dudzus, K. A. Meier, S. Recknagel, M. Hedrich and R. Matschat, *Mater. Trans. JIM*, 2002, **43**, 98–100.

7 R. Matschat, M. Czerwensky, S. Pattberg and H.-J. Heinrich, *Phys. Stat. Solidi (a)*, 2001, **189**, 107–122.

8 S. Pattberg and R. Matschat, *Fresenius' J. Anal. Chem.*, 2001, **364**, 410–416.

9 S. Pattberg, *Dissertation*, 1999, Humboldt-Universität, Berlin.

10 R. Matschat, M. Czerwensky, M. Hamester and S. Pattberg, *Fresenius' J. Anal. Chem.*, 1997, **359**, 418–423.

11 N. Jakubowski, L. Moens and F. Vanhaecke, *Spectrochim. Acta, Part B*, 1998, **53**, 1739–1763.

12 I. Rodushkin, *Application Flash Report*, Thermo Finnigan, Bremen, 2001, **E11**, pp. 1–8.

13 E. Engström, A. Sternberg, S. Senioukh, R. Edeelbro, D. C. Baxter and I. Rodushkin, *Anal. Chim. Acta*, 2004, **521**, 123–135.