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Detremination of Mercury Isotopic Profile by Inductively Coupled Plasma Mass Spectrometry: Possibilities and Limitations★

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A systematic study on the efficiency of inductively coupled plasma quadruple mass spectrometry (ICP–QMS) in determination of stable mercury isotopes profile has been conducted. Two types of effects have been observed: non-specific, which influenced all mercury isotopes, and specific, which applied only to selected isotopes. Non-specific effects were those, for which the sensitivity depended significantly on the type of mercury compound present in the solution: sensitivity decreased almost 2 and 3 times for chloride and phenylmercury $PhHg^+$ ions, respectively, compared to that for mercury in the form of inorganic Hg^{2+} as a nitrate(V). The influence of platinum and lead was specific for isotopes exposed to isobaric spectral interferences, which meant that determination of the following isotopes: ^{199}Hg, ^{200}Hg, ^{201}Hg and ^{202}Hg was unaffected. In case of ^{196}Hg, ^{198}Hg and ^{204}Hg significant isobaric interferences from ^{196}Pt, ^{198}Pt and ^{204}Pb ions were detected. It has been found that commonly used mathematical correction was not always effective and depended on the concentrations of interferents in the solution. To overcome this problem, proper detection mode (pulse or analogue) for monitoring mercury and interfering ions has been proposed.

W pracy przedstawiono wyniki badań dotyczących możliwości oznaczania stabilnych izotopów rtęci techniką kwadrupolowej spektrometrii mas z jonizacją w plazmie indukcyjnie sprzężonej (ICP–QMS). Zaobsserwowano dwa rodzaje interferencji: niespecyficzne, wpływające w równomierny sposób na wszystkie oznaczane izotopy, oraz specyficzne, wpływające na wybrane izotopy. Efekty niespecyficzne są związane z formą chemiczną, w jakiej rtęć występuje w roztworze. W porównaniu do czułości oznaczania rtęci występującej w formie nieorganicznej (Hg^{2+}) w postaci azotanów(V), czułość oznaczania zmniejsza się odpowiednio dwu- lub trzykrotnie dla chlorku rtęci(II) i octanu fenylorteci.

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★ Dedicated to Professor Rajmund Dybczyński on the occasion of his 75th birthday.

Specyficzne oddziaływania na wybrane izotopy zostały zaobserwowane w obecności platyny i ołowiu. Zaobserwowano znaczący wpływ interferencji izobarycznych pochodzących od ^{196}Pt, ^{198}Pt i ^{204}Pb na wyniki oznaczeń izotopów ^{196}Hg, ^{198}Hg i ^{204}Hg. Zastosowanie poprawki matematycznej, metody powszechnie używanej w celu eliminacji interferencji izobarycznych w oznaczeniach z zastosowaniem techniki ICP–QMS, nie zawsze było efektywne i zależało od stężenia interferentów w roztworze. W celu rozwiązania tego problemu zaproponowano wybór odpowiedniego trybu pracy detektora – plusowego lub analogowego – do pomiaru zarówno izotopów rtęci jak i interferentów obecnych w roztworze.

The knowledge of the isotopic profile of various multi-isotope elements plays an important role in understanding a variety of geological, geochemical, and biological processes in the environment since stable isotope ratios, *e.g.* N (^{15}N/^{14}N), S (^{34}S/^{32}S), C (^{13}C/^{12}C) are considered to be sensitive indicators of many natural processes [1–3]. The usefulness of investigations on mercury isotopes in geology [4] and environmental studies has been demonstrated [5–7]. Seven stable isotopes with the following natural abundances (in percentages) were used for these purposes: ^{196}Hg (0.14), ^{198}Hg (10.02), ^{199}Hg (16.84), ^{200}Hg (23.13), ^{201}Hg (13.22), ^{202}Hg (29.80), and ^{204}Hg (6.85) [8]. Martin-Doimeadios *et al*. [5] have used species-specific enriched stable isotopes to study mercury transformations (methylation, demethylation, and volatilization) in estuarine sediments under biotic and abiotic, as well as oxic and anoxic environmental conditions. Sediments were spiked with isotopically-enriched inorganic (^{199}Hg) and monomethylmercury (MM^{201}Hg) species and formation of MM^{199}Hg and degradation of MM^{201}Hg were measured simultaneously by gas chromatography (GC) with isotope dilution (ID)–ICP–MS. In numerous studies the mechanism of mercury methylation/demethylation in aquatic ecosystems has been examined using enriched isotope mercury tracers followed by ID–ICP–MS [9–11] or ID sector field (SF) ICP–MS [12] detection. Sturup *et al*. [7] have used this approach to quantify $CH_3{}^{201}Hg^+$ and $^{200}Hg^{2+}$ in zooplankton with the aim to investigate the effects of algal and zooplankton density on mercury bioaccu-mulation in a fresh water system. Sarica *et al.* [6] have studied the transfer of methyl-mercury (MeHg) from fish carcasses to scavenging leeches using ^{202}Hg-rich yellow perch.

Determination of the total content of mercury in various environmental samples can be performed with the use of *e.g.* cold vapor atomic absorption spectrometry (CV AAS) [13], graphite furnace (GF) AAS [14], or CV atomic fluorescence spectrometry (AFS) [15]. None of these methods, however, can be used to evaluate mercury isotopic profiles. For this propose, only ICP–MS can be applied as it offers high sensitivity, low detection limits (often in the ng L^{-1} range), and good precision of isotope ratio measurements (< 1% RSD). Presently, ICP–MS is considered as the most powerful elemental detector at a trace level. However, it is not free from physical (mainly memory effect) and spectral (polyatomic or isobaric) interferences [16]. It should be also stressed that for the isotopic dilution measurements it is necessary to

use isotopes, which are not exposed to any interference. In case of mercury three stable isotopes: ^{196}Hg, ^{204}Hg, ^{198}Hg can be exposed to the isobaric interferences caused by the presence of ^{196}Pt (25.3%), ^{204}Pb (1.4%) and ^{198}Pt (7.2%), respectively.

The aim of this work was to investigate the analytical performance of ICP–QMS for determination of various stable isotopes of mercury, to evaluate the mercury isotopic profiles for its inorganic and organic species, and to investigate the usefulness of the mathematical correction for elimination of interferences.

EXPERIMENTAL

Apparatus and reagents

A Sciex ELAN 6100 DRC (Perkin Elmer Sciex, USA) inductively coupled plasma quadruple mass spectrometer was used.

Inorganic mercury standard solutions were prepared by appropriate dilution of 1 g L^{-1} mercury(II) nitrate(V) stock solution (GUM, Poland) or 1 g L^{-1} mercury(II) chloride stock solution (Sigma, USA). Organic mercury solution (0.1 g L^{-1}) was prepared by dissolving an appropriate mass of phenylmercury acetate (Merck, Germany) in 100 mL of water. Standard solutions were prepared by dilutions of a stock solution before use. Lead working solutions were prepared by dilution of a 1 g L^{-1} lead nitrate(V) stock solution (Fluka, USA). Working solutions of platinum were prepared by dilution of 1 g L^{-1} platinum chloride stock solution (Merck). Rhodium standard solution was prepared by dilution of a 10 mg kg^{-1} rhodium(III) nitrate(V) stock solution (Fluka). All measurements were performed with the use of rhodium as an internal standard.

65% suprapur nitric acid(V) (m/m) (Merck) was used. In order to avoid the memory effects, the system was rinsed with 1% HNO_3 solution for 10 min after the analysis of each solution.

RESULTS AND DISCUSSION

Performance of measurements

It has been found in our preliminary experiments that the analytical performance of ICP–QMS depends significantly on the chemical form of mercury present in a sample solution. Although the optimal experimental conditions were adjusted individually for the solutions containing mercury nitrate(V) or phenylmercury acetate, a significant difference in sensitivity of mercury determination was observed. The optimal conditions are presented in Table 1.

Table 1. Apparatus and experimental conditions for determination of mercury by ICP–QMS. Bolded parameters were optimized separately for Hg^{2+} and $PhHg^{+}$

Parameter	Hg^{2+}	$PhHg^{+}$
Spray chamber	Cyclonic	
Nebulizer	Meinhard	
Torch	Quartz	
Sampler cone	Nickel – 1.1 mm	
Skimmer cone	Nickel – 0.8 mm	
Frequency	40 MHz	
Resolution	0.7 ± 0.1 u	
RF Power	1175 W	
Lens voltage	**7.5 V**	**9 V**
Analog voltage	**–1950 V**	
Puls voltage	950 V	
Plasma Ar gas flow rate	15 L min^{-1}	
Auxiliary Ar gas flow rate	1.0 L min^{-1}	
Nebulizer gas flow rate	**0.94 L min^{-1}**	**0.98 L min^{-1}**
Dwell time	100 ms	
Sweeps	5	
Number of replicates	6	
Sample uptake rate	1 mL min^{-1}	
Internal standard	Rh, 10 µg L^{-1}	

The limits of detection for all examined isotopes of mercury are listed in Table 2. As it was expected from the natural abundance data, the lowest detection limit was achieved for ^{202}Hg: 15 ng L^{-1} and 42 ng L^{-1} for Hg^{2+} and $PhHg^{+}$, respectively. Precision of the measurements was in the range 0.2–1.6% for Hg^{2+} and 1.2–3.8% for $PhHg^{+}$ (except for ^{196}Hg and ^{204}Hg – both with lower abundance, when precision was above 10%).

Table 2. Limits of detection for different mercury isotopes introduced in the form of various mercury species (ICP–QMS)

Isotope	Hg^{2+} [ng L^{-1}] as mercury nitrate(V)	$PhHg^{+}$ [ng L^{-1}]
^{196}Hg	135	297
^{198}Hg	46	95
^{199}Hg	33	63
^{200}Hg	30	74
^{201}Hg	39	66
^{202}Hg	**15**	**42**
^{204}Hg	87	129

In order to evaluate whether the isotopic profile depends on the chemical form of mercury originally present in the solution, the intensity of signals of all mercury isotopes was measured. For this purpose, standard solutions containing 10 µg L^{-1} mercury in the form of either Hg^{2+} (nitrate(V)) or $PhHg^{+}$ were prepared. The obtained profiles are presented in Figure 1. Both of them are consistent indicating that the chemical form of the analyte did not influence the ICP–QMS relative response, although its influence on the sensitivity was significant.

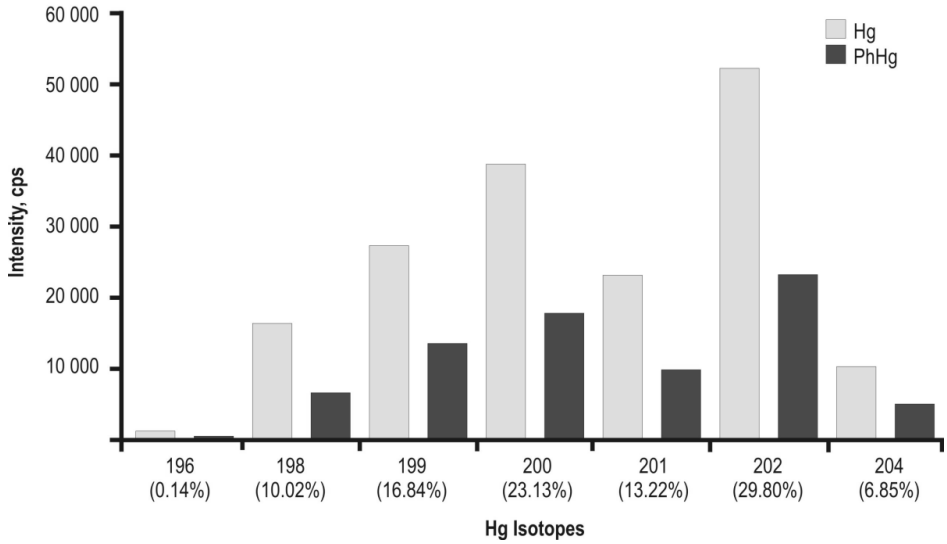

Figure 1. Intensity of signals of mercury isotopes for Hg^{2+} (as nitrate) and $PhHg^{+}$ (phenylmercury acetate); mercury concentration 10 μg L^{-1}

Spectral interferences

The main aim of this work was to evaluate the performance of ICP–QMS for determination of all stable mercury isotopes. Since the response of ICP–MS depended significantly of the chemical form of mercury present in the solution, all experiments aimed at the investigation of mercury isotopes profiles were performed separately for mercury solutions containing either Hg^{2+} or $PhHg^{+}$ ions.

As it was mentioned, in determination of various isotopes the interferences-free measurements are required in order to evaluate the processes influencing the isotopic profile and/or isotopic ratio of a selected pair of isotopes. In case of mercury, ^{196}Hg, ^{204}Hg and ^{198}Hg isotopes can be exposed to isobaric interferences from ^{196}Pt, ^{204}Pb and ^{198}Pt, respectively. In order to evaluate this phenomenon in details, a set of model solutions containing 10 μg L^{-1} Hg and the increasing concentrations of platinum and lead was prepared. Concentrations of Pt and Pb were as follows: (i) 10 μg L^{-1} Pt and 10 μg L^{-1} Pb; (ii) 350 μg L^{-1} Pt and 100 μg L^{-1} Pb; (iii) 400 μg L^{-1} Pt and 150 μg L^{-1} Pb.

The commonly used procedure to eliminate isobaric interferences in MS measurements is the mathematical correction following the appropriately designed algorithm. For example, the concentration of Pb was determined by measuring the intensity of the signal for ^{208}Pb isotope. Then, taking into account the natural abundance of all lead isotopes, the intensity of the ^{204}Pb isotope was calculated. Assuming that at the mass scale at 204 u the sum intensity of ^{204}Hg and ^{204}Pb was measured, the net

signal for ^{204}Hg should be obtained by subtraction of the calculated intensity of ^{204}Pb. The equations used for mathematical correction for both operating modes of the MS detector are given below:

(1) $I^{196Hg} = I^{sum\ (196Hg + 196Pt)} - 0.746098 \times I^{195Pt}$,

(2) $I^{198Hg} = I^{sum\ (198Hg + 198Pt)} - 0.211723 \times I^{195Pt}$,

(3) $I^{204Hg} = I^{sum\ (204Hg + 204Pb)} - 0.026718 \times I^{208Pb}$,

where I stays for the signal intensity.

The algorithm designed to eliminate the interferences from Pb and Pt was applied and tested for the solution containing 10 μg L^{-1} Hg^{2+}, 10 μg L^{-1} Pt and 10 μg L^{-1} Pb. Surprisingly, even after correction the signal intensity for all mercury isotopes, also those which should not be exposed to the interferences, was decreased by more than 50%. After careful examination of the experimental conditions and the composition of the solutions, this phenomenon was attributed to the presence of excessive chloride ions delivered to the solutions with platinum chloride, and preliminarily considered as the non-specific effect. In order to confirm this hypothesis, signal intensities of 10 μg L^{-1} mercury present either as a nitrate(V) or chloride were measured. Noticeably, no platinum chloride was present. The results presented in Table 3 confirm that chloride ions suppressed the measured signal intensity due to the formation of mercury chloride complex, which influenced the efficiency of mercury ionization.

Table 3. Calculated concentration of mercury in standard solutions containing Hg^{2+} as $Hg(NO_3)_2$ or $HgCl_2$

Isotope	Concentration of Hg(II) ± SD, μg L^{-1}	
	10 μg L^{-1} Hg^{2+} as mercury(II) nitrate(V)	10 μg L^{-1} Hg^{2+} as mercury(II) chloride
^{196}Hg	**10.2 ± 0.4**	**4.7 ± 0.4**
^{198}Hg	**10.1 ± 0.3**	**4.7 ± 0.2**
^{199}Hg	9.9 ± 0.2	4.8 ± 0.1
^{200}Hg	10.2 ± 0.1	4.9 ± 0.2
^{201}Hg	10.1 ± 0.2	4.9 ± 0.1
^{202}Hg	10.2 ± 0.1	5.1 ± 0.2
^{204}Hg	**9.8 ± 0.3**	**4.8 ± 0.4**

Therefore, further experiments on the interference effects on inorganic mercury ions were performed with the use of standard mercury solution containing $HgCl_2$. The ICP–QMS measurement system was calibrated with standard solutions containing either mercury(II) chloride or phenylmercury acetate.

For all 10 μg L^{-1} mercury solutions (with or without addition of the interfering ions) signal intensities of all mercury isotopes were measured with or without the use of mathematical correction for ^{196}Pt, ^{198}Pt and ^{204}Pb. Then, the concentration of mercury was calculated applying the external calibration; the obtained results are listed in Tables 4 and 5.

Table 4. Calculated concentration of mercury (as Hg^{2+} in the form of chloride) in the presence of the interferents with or without mathematical correction

Isotope	Concentration of Hg^{2+} ± SD, μg L^{-1}	
	10 μg L^{-1} Hg^{2+} + 10 μg L^{-1} Pt + 10 μg L^{-1} Pb (without correction)	10 μg L^{-1} Hg^{2+} + 10 μg L^{-1} Pt + 10 μg L^{-1} Pb (with correction)
^{196}Hg	**325 ± 15**	**6.5 ± 5.4**
^{198}Hg	**30.1 ± 0.3**	**9.6 ± 0.2**
^{199}Hg	9.9 ± 0.1	9.8 ± 0.2
^{200}Hg	10.1 ± 0.1	10.2 ± 0.1
^{201}Hg	10.1 ± 0.1	10.0 ± 0.2
^{202}Hg	10.0 ± 0.1	10.1 ± 0.1
^{204}Hg	**27.5 ± 0.6**	**10.4 ± 1.2**

Under the conditions described above, for both investigated mercury species good accuracy of the results was obtained using the isotopes, which were not exposed to the isotope-specific interferences (^{199}Hg, ^{200}Hg, ^{201}Hg and ^{202}Hg). In case of ^{198}Hg and ^{204}Hg, both exposed to the isobaric isotope-specific interferences, the intensity of mercury signals were strongly influenced by the presence of platinum and lead in the solution, and the respective concentrations were overestimated by the factor ranging from 3 to 5. The accurate results could be obtained only after mathematical correction. This, however, was not the case for ^{196}Hg: the signals were much higher (by the factor of 30) without correction, while they were too low after correction. This effect

was expected, since the natural abundance of ^{196}Hg is only 0.14% and that of the interfering ^{196}Pt isotope is 25.3%.

Table 5. Calculated concentration of mercury (as $PhHg^+$) in the presence of the interferents with or without mathematical correction

Isotope	Concentration of $PhHg^+ \pm$ SD, μg L^{-1}	
	10 μg L^{-1} $PhHg^+$ + 10 μg L^{-1} Pt + 10 μg L^{-1} Pb (without correction)	10 μg L^{-1} $PhHg^+$ + 10 μg L^{-1} Pt + 10 μg L^{-1} Pb (with correction)
^{196}Hg	**354 ± 18**	**7.1 ± 6.5**
^{198}Hg	**47.2 ± 0.6**	**10.7 ± 0.5**
^{199}Hg	9.9 ± 0.4	10.3 ± 0.2
^{200}Hg	10.2 ± 0.2	10.3 ± 0.2
^{201}Hg	10.2 ± 0.3	10.2 ± 0.1
^{202}Hg	10.1 ± 0.3	10.1 ± 0.2
^{204}Hg	**30.6 ± 1.4**	**10.9 ± 1.7**

The above results were obtained for the concentration of the interfering ions of 10 μg L^{-1}. By increasing the concentration of Pt and Pb it was found that the corrective algorithm was valid up to 350 μg L^{-1} for Pt and 100 μg L^{-1} for Pb. At higher concentrations the correction failed, as it is exemplified by the results listed in Table 6 and 7.

Careful examination of the measurement conditions directed our attention to the evaluation of the construction and function of the MS detector. The great advantage of ICP–MS is the relatively board dynamic range of the calibration curve. In order to perform measurements over the concentration range covering several decades, the MS analyzer was equipped with a detector working in the pulse mode for the measurements at low concentrations and in the analogue mode at higher concentrations. Under typical measurement conditions, the software selects the operating mode (pulse or analogue) depending on the number of ions reaching the detector. At low concentrations the pulse mode is used. When the number of ions exceeds 2 000 000 counts, the analog detector is automatically switched on. It should be stressed that detectors operated in pulse and analogue modes have different analytical characteristic (slope of the calibration curve). This may cause a problem, when one element (*e.g.* mer-

cury) is measured using the pulse mode and other element (*e.g.* higher concentrated platinum or lead) using the analogue mode. The threshold concentration of an element, resulting in 2 millions counts and causing an automatic change of the counting mode, varies for different elements. This is the reason why the maximum concentration corrected with the use of the mathematical algorithm was different for both interfering ions.

Table 6. Calculated concentration of mercury (as Hg^{2+} in the form of chloride) in the presence of the interferents using either pulse or analogue detector

Isotope	Concentration of Hg^{2+} ± SD, μg L^{-1}		
	10 μg L^{-1} Hg^{2+} + 350 μg L^{-1} Pt + 100 μg L^{-1} Pb	10 μg L^{-1} Hg^{2+} + 400 μg L^{-1} Pt + 150 μg L^{-1} Pb	10 μg L^{-1} Hg^{2+} + 400 μg L^{-1} Pt + 150 μg L^{-1} Pb
	pulse detector		analog detector
^{196}Hg	**859 ± 43**	**794368**	**< DL**
^{198}Hg	**9.8 ± 0.3**	**3474 ± 52**	**10.4 ± 0.5**
^{199}Hg	9.9 ± 0.1	9.8 ± 0.2	10.1 ± 0.1
^{200}Hg	9.9 ± 0.1	9.9 ± 0.1	9.8 ± 0.2
^{201}Hg	10.0 ± 0.1	9.9 ± 0.1	9.9 ± 0.2
^{202}Hg	10.0 ± 0.1	10.1 ± 0.1	9.9 ± 0.1
^{204}Hg	**10.1 ± 0.1**	**137 ± 2**	**10.2 ± 0.2**

It can be concluded from the results presented in Tables 6 and 7 that for 10 μg L^{-1} mercury, 350 μg L^{-1} Pt and 100 μg L^{-1} Pb the concentrations of all elements were measured using the pulse mode. When the concentration of the interfering elements was higher (400 μg L^{-1} Pt and 150 μg L^{-1} Pb) the analogue mode was applied. As the result of using different counting modes, much higher concentration of mercury was calculated for ^{196}Hg, ^{198}Hg and ^{204}Hg. In order to overcome this unwanted effect, various procedures were tested. The most appropriate was to program the counting process so that only the analogue mode was used for detection of mercury and interfering ions (Pt and Pb). This approach assureed that accurate concentration of mercury could be determined despite the presence of Pt and Pb (Tabs 6 and 7). The only exception was less abundant ^{196}Hg isotope; in this case, the application of the analogue detection mode failed because its low sensitivity and high background were insufficient for determination of a very low concentration.

Table 7. Calculated concentration of mercury (as $PhHg^+$) in the presence of the interferents using either pulse or analogue detector

Isotope	Concentration of $PhHg^+$ ± SD, μg L^{-1}		
	10 μg L^{-1} $PhHg^+$ + 350 μg L^{-1} Pt + 100 μg L^{-1} Pb	10 μg L^{-1} $PhHg^+$ + 400 μg L^{-1} Pt + 150 μg L^{-1} Pb	10 μg L^{-1} $PhHg^+$ + 400 μg L^{-1} Pt + 150 μg L^{-1} Pb
	pulse detector		analog detector
^{196}Hg	**831 ± 52**	**687724**	**< DL**
^{198}Hg	**9.8 ± 0.8**	**13730 ± 560**	**9.5 ± 0.7**
^{199}Hg	9.8 ± 0.2	10.3 ± 0.2	10.1 ± 0.4
^{200}Hg	9.9 ± 0.1	10.1 ± 0.2	10.2 ± 0.2
^{201}Hg	9.9 ± 0.2	10.0 ± 0.1	9.8 ± 0.2
^{202}Hg	10.0 ± 0.1	9.9 ± 0.1	10.1 ± 0.1
^{204}Hg	**9.6 ± 0.6**	**756 ± 12**	**10.4 ± 0.7**

CONCLUSIONS

The systematic studies focused on the evaluation of the performance of ICP–QMS for determination of mercury isotopic profile of its all stable isotopes were conducted. Two phenomena were observed: (i) non-specific, affecting all isotopes; (ii) isotope-specific, affecting selected isotopes exposed to isobaric interferences. It was confirmed that the sensitivity depended on the chemical form of mercury. The lowest limits of detection (15 ng L^{-1} and 42 ng L^{-1} for Hg^{2+} and $PhHg^+$, respectively) were obtained for ^{202}Hg isotope. The difference in sensitivity between nitrate and chloride mercury compounds present in the solution was also observed. In the presence of chloride the efficiency of ionization was apparently decreased and, in consequence, the sensitivity was decreased by more that 50% compared to that measured in the presence of nitric ions.

The next phenomenon investigated in this work was the influence of spectral interferences on determination of mercury isotopes. For this purpose, mathematical algorithm was used and its effect on the calculated concentration of mercury was examined. Good accuracy of determination of mercury in the solution enriched with the interfering elements (Pt and Pb) was achieved for those isotopes, which were not exposed to the interferences. In case of ^{198}Hg and ^{204}Hg, it was also possible to determine mercury after mathematical correction for ^{198}Pt and ^{204}Pb, yet careful selection of the counting mode was necessary in order to obtain acceptable recovery of the

calculated concentration. Only for the less abundant ^{196}Hg isotope it was impossible to find the proper conditions assuring its accurate counting and, consequently, accurate calculation of mercury concentration.

Conclusively, we established experimental conditions for ICP–QMS determination of mercury isotopic profile for all stable isotopes except for the less abundant ^{196}Hg. The necessary requirements were to calibrate the detector with the matrix-matching calibration solutions and to apply the mathematic correction provided that the same counting mode was used for all ions.

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