

Accurate Analysis of Trace Mercury in Cosmetics using the Agilent 8900 ICP-QQQ

Effective removal of tungsten-based interferences on five Hg isotopes using MS/MS



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Introduction

Many mercury (Hg) compounds are toxic, causing symptoms ranging from skin irritation, headaches, and tremors, through to nervous system damage, renal failure, and heart disease (1). Because Hg compounds are easily absorbed through the skin, their use in cosmetics is controlled. For example, the US Food and Drug Administration (FDA) does not allow Hg in cosmetics, except under specific conditions where there are no other safe and effective preservatives available (2). Increasingly, however, Hg has been found in cosmetic products such as skin creams, soap, and lotions sold as “anti-aging” or “skin lightening”.

Mercury is a challenging element to determine at low levels by ICP-MS. It has a high first ionization potential (10.44 eV), so is relatively poorly ionized in the plasma, leading to low sensitivity. Also, Hg has seven naturally occurring isotopes, each with relatively low % abundance, further reducing sensitivity. Many forms of Hg are also volatile, and the element’s chemistry means that it can be difficult to

stabilize in solution. To address these issues, analysts must control the acid mix used for sample preservation and rinse solutions, to avoid problems with poor linearity and long washout times. Despite these difficulties, ICP-MS can still be used successfully to perform trace-level analysis of Hg, if appropriate sample stabilization—for example with the addition of HCl—is used.

Trace-level mercury analysis is even more difficult in samples—including some cosmetics—that contain a high concentration of tungsten (W). The W matrix forms polyatomic ions WO^+ and WOH^+ that overlap all the Hg isotopes, making Hg measurement even more challenging. For example, the most abundant Hg isotopes, ^{200}Hg and ^{202}Hg , suffer interferences from $^{184}W^{16}O^+$ and $^{186}W^{16}O^+$, respectively. Collision/reaction cells (CRCs) are used successfully to control many common polyatomic interferences in conventional single quadrupole ICP-MS (ICP-QMS). However, even with CRC operation, ICP-QMS cannot reduce the WO^+ and WOH^+ interferences sufficiently to allow the accurate determination of Hg at trace levels in samples that contain a high level of W.

The superior interference removal capability of triple quadrupole ICP-MS (ICP-QQQ) was investigated for this application. ICP-QQQ has dramatically improved the performance of reaction cell methods by using two mass-selection steps (MS/MS), one before and one after the CRC. In MS/MS, reaction chemistry in the CRC is controlled and consistent because only the target analyte mass enters the CRC. This capability offers a much more predictable and reliable approach to resolving interferences on a wide range of elements, particularly in complex and variable samples (3–5).

In this study, an Agilent 8900 ICP-QQQ was used for the measurement of Hg in a tungsten-rich cosmetic sample.

Experimental

Standards and samples

Mercury standards were prepared in 0.5 % high purity hydrochloric acid (TAMA-Pure-AA-100, Kanagawa, Japan).

A tungsten-rich cosmetic toning lotion was bought from a local store in Shanghai. The liquid sample was weighed to the nearest 0.100 g, and then diluted 100-fold with de-ionized water acidified with 0.5 % HCl to ensure Hg stability. The sample was shaken for a couple of minutes to ensure it was fully homogenized. The concentration of W in the original cosmetic sample was about 4000 mg/kg (ppm), as determined by ICP-QQQ in a diluted sample. Therefore, the W matrix in the sample as analyzed was about 40 mg/L (ppm) after the 100x dilution.

Instrumentation

An Agilent 8900 Standard configuration ICP-QQQ was used. The instrument was fitted with the standard sample introduction system comprising a glass concentric nebulizer, quartz double-pass spray chamber, quartz torch with 2.5 mm id injector, and Ni interface cones. The ICP-QQQ was operated in no gas mode, with He cell gas, and with O_2 cell gas in both single quad (SQ) and MS/MS modes. The main operating conditions are shown in Table 1.

Table 1. 8900 ICP-QQQ operating conditions.

Parameter	No gas	He	O_2	O_2
Acquisition mode	Single Quad			MS/MS
RF power (W)	1550			
Sampling depth (mm)	8.0			
Carrier gas flow rate (L/min)	0.8			
Make-up gas flow rate (L/min)	0.4			
Spray chamber temp. ($^{\circ}C$)	2			
He cell gas flow rate (mL/min)	-	5.0	-	-
O_2 cell gas flow rate (mL/min)	-	-	-	0.9

Results and Discussion

As the most abundant isotope, ^{202}Hg is selected as the preferred isotope for ICP-MS measurements. However, some analysts select ^{201}Hg instead (or as well), as the 201 isotope has proportionally lower W-based interference. The Hg calibration was prepared in a matrix of dilute (0.5 to 1.0%) HCl to ensure that the Hg remained stable in solution as a Cl-complex. The calibration plots for ^{201}Hg and ^{202}Hg are shown in Figure 1. The figures of merit—linearity, detection limit (DL), and background equivalent concentration (BEC)—taken from the ^{202}Hg calibration are presented in Table 2.

Table 2. DL, BEC, and R value of the calibration curve of ^{202}Hg in dilute HCl determined in four different cell modes.

	8900 calibration performance figures of merit for ^{202}Hg			
	No gas	He	O_2 Single Quad	O_2 MS/MS
R	0.997	0.999	0.999	0.999
DL ($\mu g/L$)	0.002	0.001	0.002	0.002
BEC ($\mu g/L$)	0.011	0.008	0.003	0.003

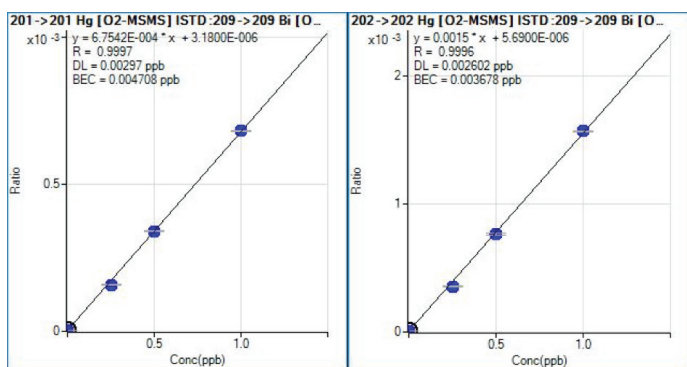


Figure 1. Calibration plots for ^{201}Hg and ^{202}Hg , demonstrating good sensitivity and linearity due to effective stabilization of Hg by the addition of HCl.

ICP-MS/MS reaction mechanism used to resolve W-based interferences on Hg

The general reaction mechanism using MS/MS mode with O_2 cell gas to resolve the WO^+ and WOH^+ interferences on Hg is shown in Figure 2. Since ^{200}Hg suffers the most serious polyatomic ion overlaps, the reaction mechanism is illustrated using the example of the $^{184}\text{W}^{16}\text{O}^+$ overlap on $^{200}\text{Hg}^+$. Q1 is set to m/z 200, so $^{200}\text{Hg}^+$ and WO^+ ions at m/z 200 pass through Q1 and enter the CRC. WO^+ reacts with the O_2 cell gas to form WO_2^+ and WO_3^+ , shifting to higher masses. The $^{200}\text{Hg}^+$ ions do not react with the O_2 cell gas and so remain at m/z 200. By setting Q2 to m/z 200, $^{200}\text{Hg}^+$ ions pass to the detector free of interference. The same reaction mechanism is effective at resolving the WOH^+ interferences, as WOH^+ also reacts with the O_2 cell gas to form higher-order product ions.

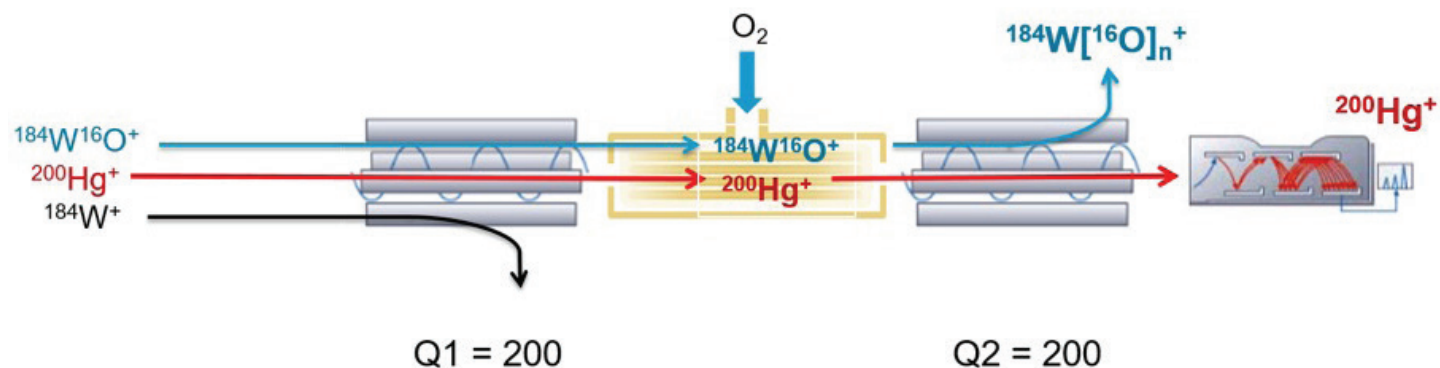


Figure 2. Reaction mechanism in MS/MS mode with O_2 cell gas for removal of WO^+ overlap to allow on-mass detection of Hg in a tungsten matrix. The same mechanism is also effective at resolving WOH^+ overlaps.

Multiple isotope analysis study

To investigate the effectiveness of interference removal in the different cell gas modes, a $1 \mu\text{g/L}$ (ppb) Hg spike was added to the diluted W-rich cosmetic lotion sample. The five most abundant Hg isotopes were measured in the four different cell gas modes, and the isotopic ratios calculated. Comparing the measured isotope ratios with the theoretical natural ratios gives an excellent indication of the effectiveness of the interference-removal on each isotope. This capability is important for many ICP-MS applications, where the results calculated from a second isotope can be used to confirm the concentration reported using the primary or preferred isotope. Performing “confirmatory measurements” is recommended or required in several regulated methods across the environmental, food, and pharmaceutical industries. This approach is analogous to the use of “qualifier ions” in organic mass spectrometry.

The isotope ratios for several Hg isotope pairs measured in the W-rich cosmetic sample using the four cell gas modes are presented in Table 3. These results show that MS/MS mode with O_2 cell gas gives measured Hg ratios that are virtually identical to the theoretical natural ratios. O_2 in MS/MS mode is much more effective than the other modes for the removal of the tungsten oxide and hydroxide polyatomic interferences. The effective removal of the WOH^+ overlap on ^{201}Hg is illustrated by the accurate ratios obtained for the $^{200}\text{Hg}/^{201}\text{Hg}$ ratio in MS/MS mode using O_2 cell gas.

Table 3. Hg isotope ratios in tungsten-rich sample measured in different cell modes.

Hg ratio	Natural value	8900 measured results			
		No gas	He	O ₂ Single Quad	O ₂ MS/MS
198/199	0.591	1.738	1.769	1.435	0.598
198/200	0.432	0.831	0.823	0.739	0.43
200/201	1.75	49.4	61.4	7.75	1.76
201/202	0.441	0.022	0.017	0.126	0.445

As a further illustration of the ability of MS/MS to resolve interferences on multiple Hg isotopes, a scan spectrum comparison was made using on-mass measurement (Q1 = Q2). The mass range of the Hg isotopes was acquired for a simple Hg standard (1 µg/L) and a solution containing the same concentration of Hg spiked into a high W matrix (10 mg/L). The overlaid spectra are shown in Figure 3, together with the template indicating the natural abundance of the Hg isotopes. The spectra show that the measured isotopic abundances match the natural Hg isotope pattern in both samples. This confirms the ability of MS/MS mode with O₂ cell gas to remove the W-based overlaps caused by the high W matrix in the second sample.

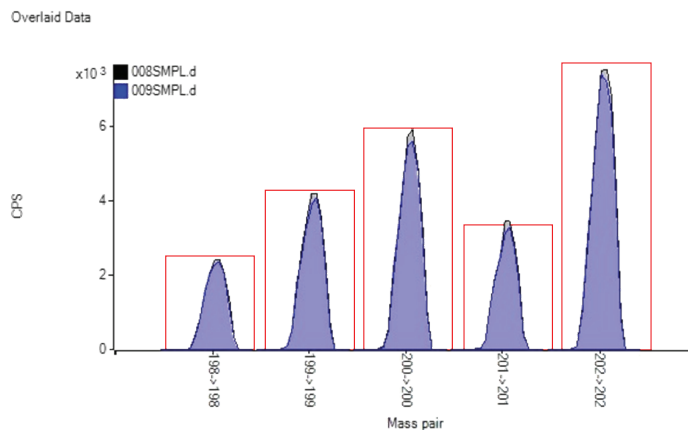


Figure 3. Hg isotopes with W matrix (blue shading) and without W matrix (gray shading), confirming accurate Hg isotope abundances and effective removal of W-based interferences on all Hg isotopes by ICP-QQQ with MS/MS.

Hg in tungsten-rich samples

Hg was measured in a tungsten-rich cosmetic sample using four different cell gas modes. The five most abundant isotopes of Hg (198, 199, 200, 201, and 202) were used for quantitation, giving five independently calibrated results for total Hg. The results for Hg in the original cosmetic sample, corrected for the 100 times dilution, are shown in Table 4.

Table 4. Apparent Hg concentration (µg/kg) in tungsten-rich cosmetic sample, quantitated independently using five isotopes. The data shows errors due to the contribution from WO⁺ and WOH⁺ overlaps in no gas, He, and O₂ (SQ) cell modes.

Cell mode	Hg result based on isotope				
	198	199	200	201	202
No gas	267000	87200	136400	4770	98700
He	173200	57700	90700	2460	66500
O ₂ Single Quad	772	249	399	2.8	288
O ₂ MS/MS	2.1	1.8	2.4	1.5	1.7

Matrix-based interferences affect different isotopes of an analyte to different degrees, so giving different errors in the quantitative results calculated from each isotope. Comparing the elemental concentrations calculated from the different isotopes of an element can therefore be used to identify whether the reported concentrations were affected by interferences. The reported Hg concentrations in MS/MS mode with O₂ (~2 µg/kg in the original sample, or 0.02 µg/L in the 100x diluted solution) are much lower than the results reported using the other cell modes. Also, the good agreement between the results obtained for the five isotopes in O₂ (MS/MS) mode shows that this mode can simultaneously remove polyatomic interferences from all five Hg isotopes. These results contrast with the other modes, where incomplete removal of interferences from most of the isotopes led to erroneously high values and large differences between the results calculated using the different isotopes. The reported concentration of 2.8 µg/kg obtained for ²⁰¹Hg using O₂ cell gas in single-quad mode shows that the WOH⁺ interference could be reduced reasonably effectively. However, the other isotopes gave variable results in O₂ (SQ) mode, so the ²⁰¹Hg result could not be verified by comparing it with a second, qualifier isotope. The data in Table 4 shows that, even when a suitable reaction gas is identified, MS/MS is essential for full control of the reaction chemistry.

Spike recovery test

A spike recovery test was carried out to further evaluate the interference removal capability and matrix tolerance of the method. Since ^{200}Hg suffers the most serious polyatomic ion overlaps, it was selected as the target mass for the spike recovery test.

A 30 ppt spike of Hg was added to the diluted cosmetic lotion sample. The spike recovery in O_2 (MS/MS) mode was 104%, confirming the interference removal capability and matrix tolerance of the method (Table 5).

Table 5. 30 ppt Hg spike recovery results in different cell gas modes.

	Mode	Sample ($\mu\text{g/L}$)	Spike recovery (%)
200 Hg	No gas SQ	1364	6635
200 Hg	He SQ	906	879
200 Hg	O_2 SQ	3.99	216
200 -> 200 Hg	O_2 MS/MS	0.024	104

Conclusions

The Agilent 8900 ICP-QQQ operating in MS/MS mode with O_2 cell gas is highly effective for the removal of tungsten oxide/hydroxide polyatomic interferences on the five major Hg isotopes.

- Hg was measured accurately and consistently at trace levels in the presence of W using an MS/MS on-mass method with O_2 reaction cell gas.
- Compared to conventional single quadrupole ICP-MS, ICP-MS/MS reduced interferences by more than two orders of magnitude.
- The ICP-MS/MS method easily meets the requirements of trace level Hg analysis in tungsten-rich cosmetic samples.

References

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