Interference-free Measurement of Trace Mercury in Tungsten-rich Cosmetic Sample using ICP-QQQ

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Introduction

ICP-MS is the most widely used atomic spectrometry technique for the measurement of trace elements. Analysis of trace level Hg in cosmetic sample is routine test by ICP-MS. However, large amounts of tungsten in the cosmetic samples makes mercury measurement be challenged, due to the serious poly-atomic interference from WO^+ and WOH^+. Normally, collision or reaction gas could be introduced into the cell to remove the interference. Unfortunately, tremendous WO^+ and WOH^+ that formed in the plasma could not be completely eliminated by conventional single-quad ICP-MS. Therefore, in this paper, we investigated several types of cell gas coupled with MS/MS mode to achieve the free-interference measurement. Q1 is operated as the first mass filter, which could select the target mass, and reject all the other ions. Reaction/collision cell coupled with the Q2, could prevent the poly-atomic interference, just like WO^+ and WOH^+, from overlapping Hg^+. With this function, we can easily control the reaction process and enhance the interference removal capability.

In this study, Agilent 8900 ICP-QQQ, as the tandem mass instrument, was used for the Hg analysis in this tungsten rich sample. And oxygen has been demonstrated as the most powerful cell gas operated at tandem MS mode. More abundance isotopes of Hg were measured, and the results could be achieved at 20 ng/L for Hg in the cosmetic sample containing about 200 mg/L W. Single-quad mode with O_2 as reaction gas was also studied, and almost two orders of magnitude could be improved by MS/MS mode. With 1 µg/L of Hg spike, the recoveries ranging from 105 to 111% could be achieved by oxygen combining with MSMS mode. The isotope peak pattern generated by ICP-QQQ perfectly match the natural abundance. That could be taken as the demonstration for the interference-free measurement of Hg in tungsten-rich samples.

Experimental

ICP-MS/MS

Agilent 8900 series ICP-MS/MS was used in this paper, with a standard configuration, including oxygen, helium, hydrogen and ammonia cell gas. Tungsten-rich cosmetic samples were applied for the mercury analysis.

Sample preparation

Mercury standards were prepared in trace-level of hydrochloric acid (TAMA-Pure-AA-100, Kanagawa, Japan). Weigh the samples to the nearest 0.100g, and dilute the samples with Milli-Q deionized water at 100 times. Agitate the mixture for couples of minutes for sample well distribution. Before introducing to ICP-MS, make filtration through a membrane filter to remove visible solid material.

ICP-MS Operating Parameters

Agilent 8900 Triple Quadrupole ICP-MS #100 with 2.5 mm injector torch. RF = 1550W, SD = 8.0mm, CRGS = 0.8L/min, MUGS = 0.4L/min, Spray Chamber Temp. = 2 ℃

Four modes were used in this study, for investigating the different interference removal capability. The multi-isotopes of Hg were studied in this paper for demonstration of the interference-free measurement.

	W				
Mass	180	182	183	184	186
%	0.12	26.5	14.31	30.64	28.43
☐	☐	☐	☐	☐	☐

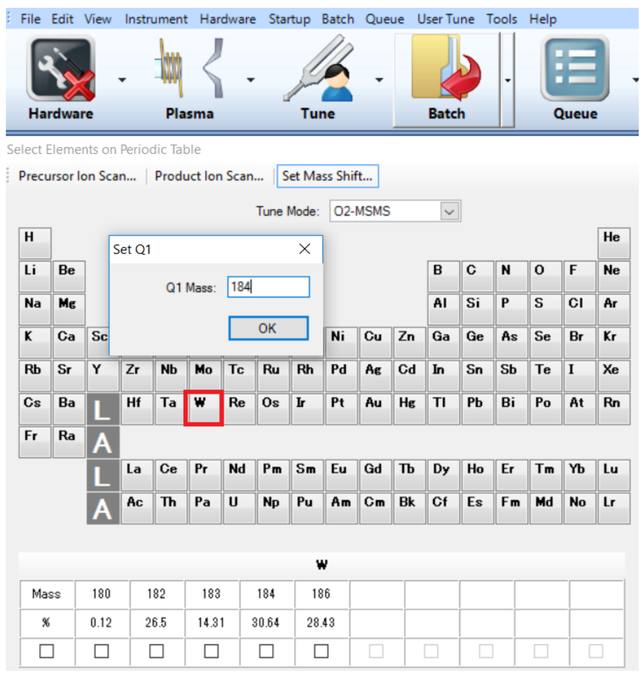
0, OH

	Hg						
Mass	196	198	199	200	201	202	204
%	0.15	9.97	16.87	23.1	13.18	29.86	6.87
☐	☐	☐	☐	☐	☐	☐	☐

Experimental

Product ion scan

To make the mechanism of interference removing clearly, the function of product ion scan was applied in this study.



In this process, the analyte and interference ions, before and after introduction into cell, could be more easily tracked by ICP-MS/MS.

Results and Discussion

Isotope fingerprint study

To verify the interference removal capability, multi-isotope has been selected for investigation. Isotope ratio could be taken as great tool for checking the isotope fingerprint.

Table 1. Isotope ratio of Hg in tungsten-rich sample

	198/199	198/200	200/201	201/202
Natural	0.591	0.432	1.75	0.441
8900 ICP-MS/MS Results				
No gas	1.738	0.831	49.4	0.022
He	1.769	0.823	61.4	0.017
O_2-SQ	1.435	0.739	7.75	0.126
O_2-MSMS	0.598	0.430	1.76	0.445

As Table 1 shows, O_2 as reaction gas with MS/MS mode, presents more effective than single-quad (SQ) mode for the oxide-related polyatomic interference removal.

The isotope of 201 are free from WO overlapping, but some amount of WOH should be the target interference ions. With He as collision gas and O_2 as reaction gas, 8900 ICP-MS/MS was operated at single-quad mode, the isotope ratio of $^{200}Hg/^{201}Hg$ matched much better with natural ratio in oxygen mode. However, without Q1 mass filter, large amounts of W went through the cell, and part of them formed the WO, overlapping at Hg.

Q1 removes unwanted precursor ions like W^+ to prevent unexpected reaction products from interfering. The oxygen atom affinity is larger than mercury, but smaller than tungsten oxide atom. So oxygen could move to tungsten, forming WO_n. Although the isotope of ^{204}Hg is free from $W^{16}O$, isobar from ^{204}Pb would overlap at Hg. Even though suffering from serious WO interference, ^{200}Hg could achieve ppt-level result by O_2 with MS/MS mode.

Results of Hg in tungsten-rich sample

Five different isotopes of Hg were investigated in this study, and the result was shown in the table 2.

Table 2. Results of Hg in tungsten-rich sample (µg/L)

	198	199	200	201	202
No gas	2670	872	1364	47.7	987
He	1732	577	907	24.6	665
O_2-SQ	7.72	2.49	3.99	0.028	2.88
O_2-MSMS	0.021	0.018	0.024	0.015	0.017

From table 2, all the investigated isotopes could be achieved almost the same result, about 0.02 µg/L, under the oxygen with MS/MS mode. Even though the conc. of Hg calculated by isotope 201 is 0.028 µg/L in single-quad oxygen mode, the interference from WHO was almost reduced. However, the results obtained by the other four isotope in this mode could not get agreement with 0.028 µg/L. That means only with oxygen gas operated at MS/MS mode, the results could be verified by the same conc. of Hg in this sample, even calculated by five different isotopes.

Results and Discussion

Capability of interference removal by ICP-QQQ

Hg and WO undergo chemical reaction with O_2 as follows:

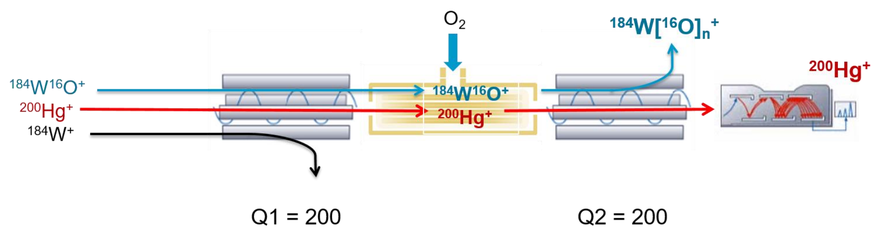


Fig.1 Mechanism of MS/MS mass-shift, using O_2 for the detection of Hg in high-tungsten matrix

O_2 on-mass method was applied to Hg measurement; O_2 flow rate = 0.9 ml/min, Octpole Bias = -5.0 V, WO^+ reacts with O_2 molecule and forms multi-oxide product ions WOO^+, $WOOO^+$, etc. thereby Hg is detected as Hg^+ for interference-free.

Table 3. Results of the spike recovery for Hg

	Mode	Sample (µg/kg)	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-MSMS	0.024	104

The sample with 100 times dilution, was introduced into the ICP-MS/MS. The spike recovery test was evaluated for the interference removal capability and matrix tolerance. The mass number 200 suffers the most serious polyatomic ions overlapping, so it is selected as the target mass for spike recovery test. From the table 3, oxygen as reaction gas with MS/MS mode presents more effective in removing the tungsten oxide interference. ICP-MS/MS, there are two mass filters in the standard configuration. Different from conventional single-quad ICP-MS, Q1 could prevent most the tungsten ions into the collision/reaction cell, and only limited amounts of tungsten oxide could be formed in the plasma. And then WO^+ came through into the reaction cell, multi-oxide product ions could be obtained in the cell. Therefore, with on-mass mode, Hg could be easily get the interference-free measurement at Q2, due to the elimination of WO from octopole cell.

Here, the verification of result could be achieved by the measured conc. of Hg and spike recovery. Excellent recovery means totally eliminated the WO overlapping at Hg and fabulous matrix tolerance. However, which approach can provide the detail information of the reaction product ions for WO? Fortunately, the function of product ion scan could make this process clearly. Fix Q1 at mass 184, and operate Q2 at full scan mode. The product ions produced from W ranging from WO to multi-oxide tungsten ions. It's extremely important to get this information, especially for the further demonstration. The product ion scan result provided the mechanism of interference-free analysis.

Conclusions

As can be seen, MS/MS mode presents more effective than single-quad (SQ) mode for the oxide-related polyatomic interference removal.

- Using the 8900 ICP-MS/MS with reaction gas on-mass mode, Hg could be measured at original mass. And WO can be transferred as their multi-oxide ions and cluster product ions, preventing intense oxide ions interference.
- In compared to conventional ICP-MS (Single-Quad MS), it is more than two orders of magnitude lower interferences obtained by ICP-MS/MS.
- For the serious polyatomic interference, 8900 ICP-QQQ can easily to meet the requirements of trace level Hg analysis in cosmetic samples, even though in extremely high level concentration of W matrix.

References

References: Roboto Light 11 pt Black type. Text is left justified. Line spacing is .9. Paragraph spacing is 6 pt.

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