Efficient Removal of Polyatomic Ions by ICP-MS Equipped with Novel Reaction Cell: Examples of Highly Purified Chemicals Used for Semiconductor

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Introduction

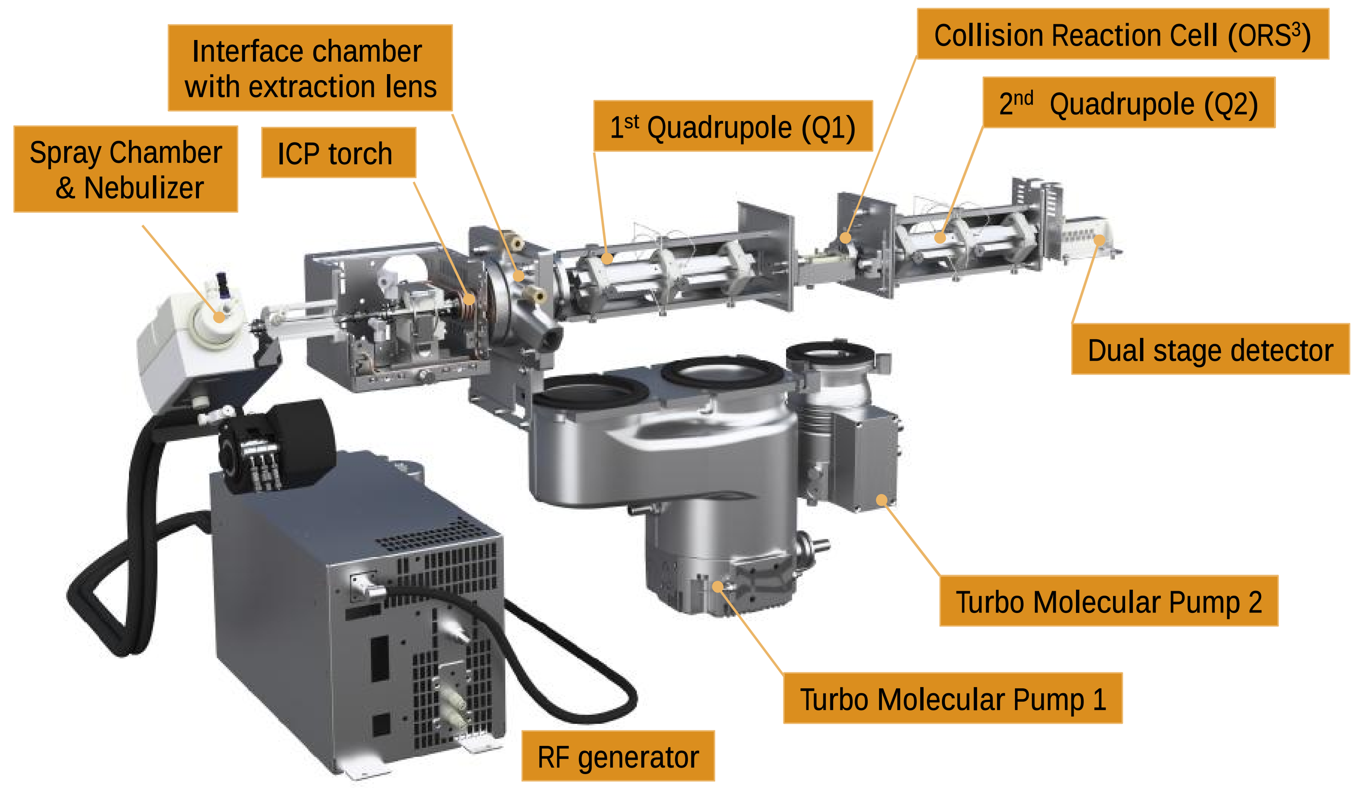

Figure 1. Configuration of Agilent ICP-QQQ

ICP-MS equipped with collision/reaction cell is now the standard analytical technique for metallic impurities of materials including environmental samples, food, rocks, drinking water, chemicals and so on. However, spectral interferences still create problems when determining several elements. Dilution or use of minor isotope was the best choice to avoid such problems, however, semiconductor industries in particular require higher detectability of elements in complex but highly pure chemicals. For example, on determination of Ti in H_2SO_4, ^{47}Ti is chosen and ^{46}Ti is used for the analysis of H_3PO_4. So what isotope of Ti should be used for analyzing the mixture of H_2SO_4 and H_3PO_4? Another example is phosphorus. P has only one isotope of ^{31}P which is susceptible to common HNO_3 spectral interference. Use of high resolution ICP-MS was the solution.

New technology of ICP-QQQ-MS by Agilent can solve these problems. Examples are shown here.

Experimental

Instrument

ICP-MS illustrated in the left figure was used. Hydrogen, oxygen and ammonia gases were chosen as reaction cell gas. PFA nebulizer, 2.5mm injector (quartz or platinum) torch and spray chamber (quartz or PFA) were the sample introduction devices. The sample solution was introduced by self aspiration of the nebulizer. The sampling cone and skimmer cone were made of platinum with nickel. Metallic impurities of all the chemicals used for analysis were guaranteed to be less than 100ppt by manufacturers.

Operating Conditions

- RF power: 1600 W
- Sampling depth: 8 mm
- Carrier gas flow rate: 0.8 L/min (Uptake is approx. 200µL/min)
- Makeup gas flow rate: 0.4L/min
- ORS gas: 100% H_2, 10% NH_3 balanced with He and 100% O_2
  Purity of ORS gases was higher than 99.995%.

Results and Discussion

BEC of Phosphorus in UPW (0.8% HNO_3), ppb

H_2		NH_3 with H_2		O_2	
^{31}P / $^{31}PH_3$	0.07	^{31}P / $^{31}P^{14}NH_3$	0.12	^{31}P / $^{31}P^{16}O$	0.10
^{31}P / $^{31}PH_4$	0.08	^{31}P / $^{31}P(NH_3)_2$	0.10	^{31}P / $^{31}P^{16}O^{16}O$	0.20
H_2 flow rate	10 scc/min	NH_3 flow rate H_2 flow rate	0.5 scc/min 10 scc/min	O_2 flow rate	5 scc/min

Q1 was set at mass 31 to introduce ^{31}P and isobaric polyatomic ions, and Q2 was set at different masses to pass only product ions. Addition of hydrogen to the ammonia reaction cell enhanced the production of PNH_3 and $P(NH_3)_2$ ions.
Spectral interference by nitric acid which was the major problem of P detection by conventional ICP-MS, was completely eliminated as shown in Figure 2.

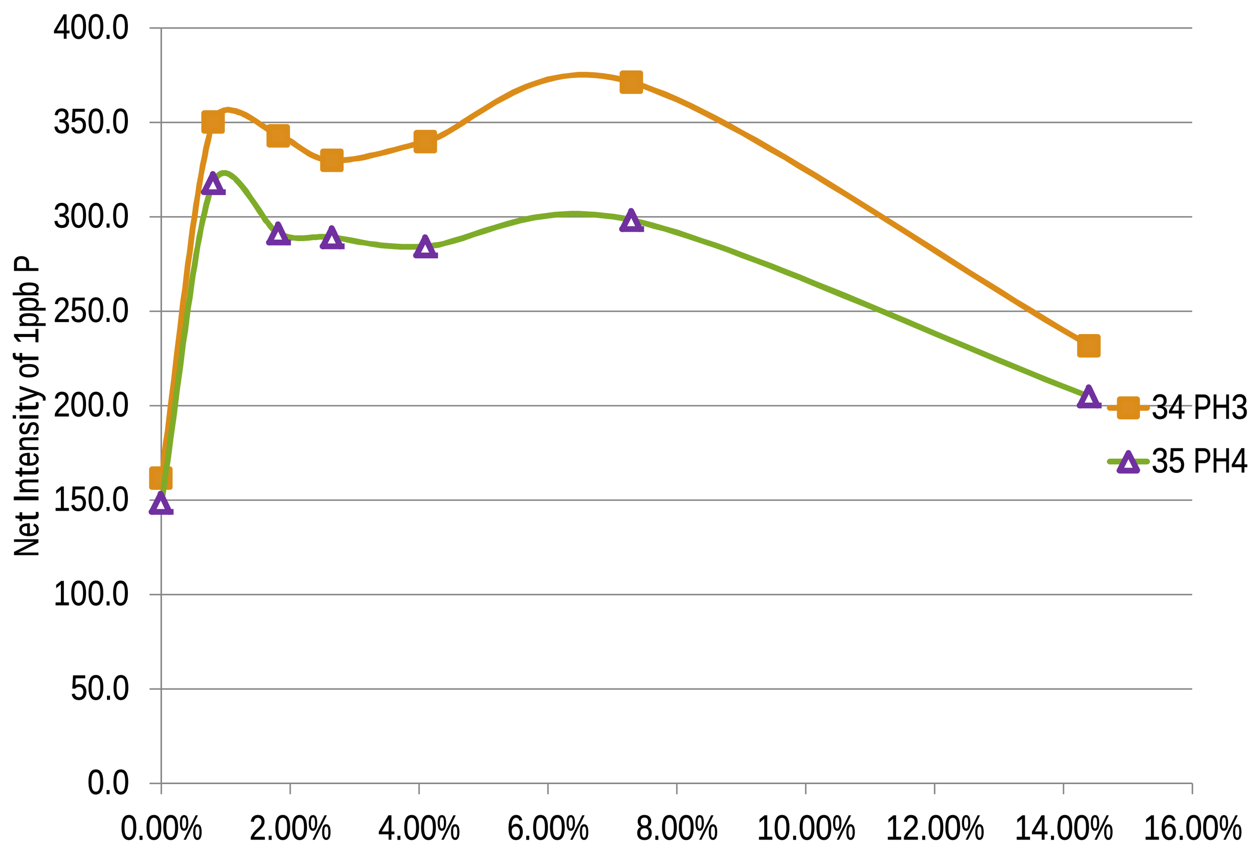

Figure 2. Effect of HNO_3 Concentration on P signal

20% Hydrochloric Acid

The major spectral interferences found in Cl-matrices solution are $^{35}Cl^{16}O$ on ^{51}V, $^{35}Cl^{16}OH$ on ^{52}Cr, $^{37}Cl^{37}Cl$ on ^{74}Ge and $^{40}Ar^{35}Cl$ on ^{75}As. BECs and DLs of these elements shown below were obtained from 20% HCl..

	V	Cr	Ge		As
ORS Gas	NH_3	NH_3	O_2	O_2	O_2
Q1 / Q2	^{51}V / ^{51}V	^{52}Cr / $^{52}Cr(NH_3)_2$	^{74}Ge / $^{74}Ge^{16}O$	^{74}Ge / $^{74}GeO_2$	^{75}As /$^{75}As^{16}O$
BEC, ppt	0.4	13	4	3	20
DL, ppt	0.4	8	1.5	2.5	2.5

10x Diluted Sulfuric Acid (9.8%)
BEC of phosphorus obtained from 9.8% H_2SO_4 by QQQ reaction mode was compared with that of conventional He collision mode. NH_3, H_2 and O_2 reaction gases provided similar BECs.

Mode	NH_3		H_2	O_2
Q1 / Q2	^{31}P / $^{31}PNH_3$	^{31}P / $^{31}P(NH_3)_2$	^{31}P / $^{31}PH_4$	^{31}P / $^{31}P^{16}O$
BEC, ppb	0.16	0.15	0.16	0.14
7700s He	20 ppb			

H_2SO_4 is well known to create troublesome polyatomic ions which make it difficult to determine some elements at ppt level. Spectral interferences of $^{32}S^{16}O$ on ^{48}Ti and of $^{34}S^{16}OH$ on ^{51}V could be avoided by using NH_3 gas reaction for determination. However, appropriate reactions are not found as of now to create product ions of Cr and Zn. For determination of these elements, He collision is still the best choice to avoid spectral interferences of $^{36}S^{16}O$ and S_2 ions.

	^{48}Ti	^{51}V	^{52}Cr		^{68}Zn	
Mode	QQQ reaction	QQQ reaction	QQQ reaction	He collision	QQQ reaction	He collision
Product ion	TiNH	V	$CrNH_3$	Cr	$ZnNH_3$	Zn
BEC, ppt	2	0.1	50	6	6.5	1
7700s He	60	3	8		1	

2000ppm Si matrix
Most manufacturers of semiconductor devices routinely analyze Si VPD samples which sometimes contain high Si matrix. Si matrix as high as 2000ppm produces polyatomic ions of Si that interfere with P and Ti. Elimination of these interferences are shown below. Low uptake nebulizer (50µL/min) and robust plasma condition were applied. Si solution was made from Si wafer, but the solution may have been contaminated.

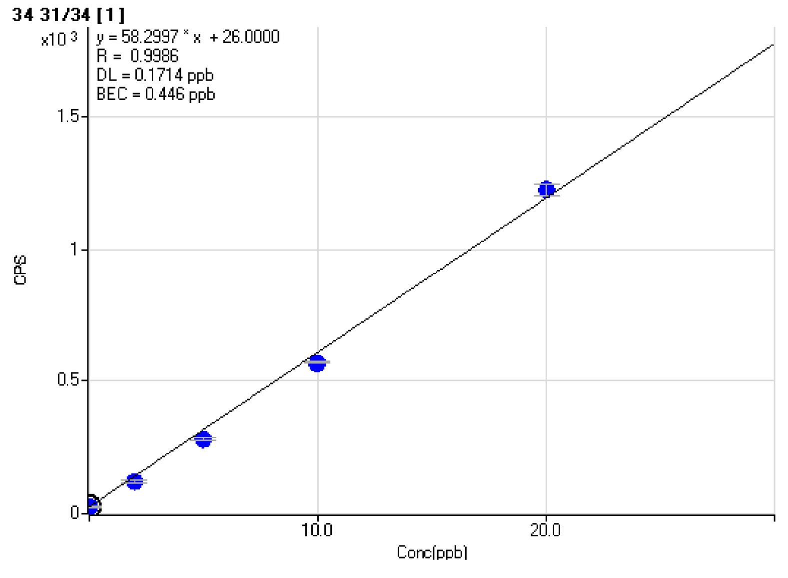

Figure 3. Calibration Curve of Phosphorus

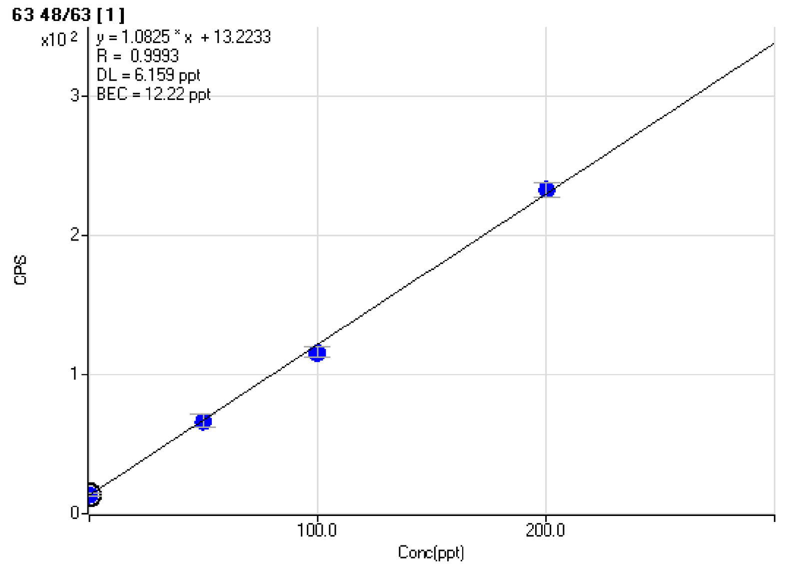

Figure 4. Calibration Curve of Titanium

Conclusions

ICP-QQQ-MS works very well to avoid spectral interferences which could not be solved by conventional collision/reaction technology. It makes it possible to determine ultra trace impurities even in complex mixture of high purity chemicals such as HF, HNO_3, H_2SO_4 and H_3PO_4.