

Sub-ppb detection limits for hydride gas contaminants using GC-ICP-QQQ

Application note

Semiconductor and petrochemical

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Introduction

Hydride gases, such as phosphine and arsine, are important contaminants in process chemicals used in both the petrochemical and semiconductor industries. For example, the presence of phosphine, arsine, hydrogen sulfide and carbonyl sulfide in polymer grade ethylene or propylene can have a deleterious effect on catalysts used in the production of polypropylene plastics. Accurate data on the concentrations of these contaminants at trace levels enables prediction of catalyst lifetime and minimizes production downtime.

In the semiconductor industry, phosphine is used as a precursor for the deposition of group III-V compound semiconductors, and as a dopant in the manufacturing of semiconductor devices, such as diodes and transistors. In the case of group III-V compound materials, such as indium phosphide (InP), absence of other hydride dopant impurities e.g., silane, germane or hydrogen sulfide (and moisture) is critical, as they can have a profound effect on the performance of the final device. In particular, incorporated sulfur from hydrogen sulfide and carbonyl sulfide may affect the electrical properties of



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the device, such as carrier concentration and electron mobility. In the case of arsine, which is used in the manufacture of high electron mobility transistors (HEMTs) and field effect transistors (FETs), product performance can be adversely affected by the presence of germane.

To date, measurement of these contaminants at ppb levels has been sufficient, but increasing competition within the industry and evolving performance criteria are pushing specifications ever lower. In addition, high purity gas manufacturers often require analytical detection limits 5–10 times lower than reported specifications. Earlier generation quadrupole ICP-MS (ICP-QMS) detectors were capable of measuring sulfur and silicon species at the 10 ppb level. More recently, the Agilent 7900 ICP-MS has demonstrated the ability to measure these elements at the 1–2 ppb level. In anticipation of increasing industry demand for even lower levels, a new high sensitivity GC-ICP-MS method using the Agilent 8800 Triple Quadrupole ICP-MS (ICP-QQQ) was developed for this application.

Experimental

Instrumentation

An Agilent 7890 GC was coupled to an Agilent 8800 ICP-QQQ using the Agilent GC-ICP-MS interface. The GC operating parameters given in Table 1 were also used for a parallel GC-ICP-MS study using an Agilent 7900 ICP-MS.

Table 1. GC operating parameters

Parameter	Setting
Column	100 meter x 0.53 mm x 5.0 μ m DB-1
Flow	Pressure control isobaric @ 20 psig
Column exit pressure	4 psig
Temperature	Isothermal ambient
Gas sampling valve and sample size	6 port valve with 400 μ L loop

The 8800 ICP-QQQ features two quadrupole mass filters (Q1 and Q2), situated either side of the Octopole Reaction System (ORS³) collision/reaction cell (CRC). In MS/MS mode, Q1 operates as a mass filter, allowing only the target analyte mass to enter the cell, and rejecting all other masses. Because plasma, matrix and all non-target analyte ions are excluded by Q1, the reaction processes in the ORS³ are precisely controlled

and consistent, so accurate measurements can be performed even in complex, high matrix samples, while sensitivity is significantly increased. The ORS³ cell can be pressurized with either a collision gas to remove polyatomic ions by kinetic energy discrimination (KED), or by collision-induced dissociation (CID), a reactive gas to selectively react with either the interfering or the target ion to attain interference-free measurement, or a combination of both.

In this study, the 8800 ICP-QQQ was operated in MS/MS mass-shift mode using oxygen as the reaction gas for the measurement of Ge, As, P, and S. Hydrogen cell gas mode was used for the on-mass measurement of the primary isotope of Si at m/z 28. Tuning conditions were almost identical for the two modes, the only differences being in the KED voltage and the cell gas flow.

Table 2. Agilent 8800 ICP-QQQ operating conditions

	O ₂ mode	H ₂ mode
RF power (W)	1350	
Sample depth (mm)	8.4	
Argon carrier (makeup) gas flow (L/min)	0.85	
Extract 1 (V)	-150	
Extract 2 (V)	-190	
Omega bias (V)	-120	
Omega lens (V)	2.2	
Cell entrance (V)	-50	
Cell exit (V)	-60	
Kinetic Energy Discrimination (V)	-4	0
Cell gas flow (mL/min)	0.35	5.0

Reagents

Gas standards of silane, phosphine, germane, arsine (all balanced with H₂), and hydrogen sulfide and carbonyl sulfide (balanced with Ar) were supplied by Custom Gas Solutions at a nominal value of 10 ppmv. These standards were dynamically diluted in helium using a pressure/fixed restrictor based diluter supplied by Merlin MicroScience.

Results and discussion

Low level phosphine analysis

The purpose of this experiment was to establish a detection limit for phosphine (PH₃) using GC-ICP-QQQ under ideal conditions. Q1 was set to *m/z* 31 (the precursor ion ³¹P⁺) and Q2 was set to *m/z* 47 to measure the reaction product ion ³¹P¹⁶O⁺. Since the eluting peaks are relatively narrow, with duration of no more than ~12 seconds, a maximum of 1 second was set for the total scan time. For the single element analysis of phosphine (measured as PO⁺), an integration time of 1.0 second was used. A multi-point calibration curve was generated for PH₃ at concentrations of 8.2, 18.8 and 50.8 ppb (Figure 1). This covers the representative concentration range required for the measurement of this contaminant.

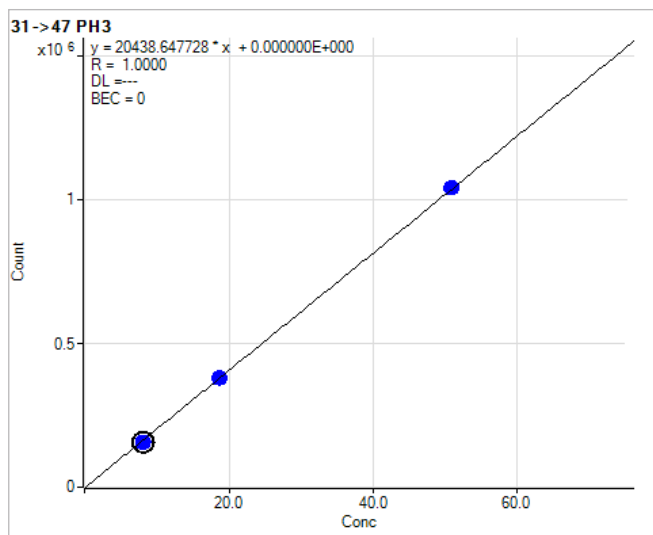


Figure 1. Phosphine calibration curve with an R value of 1.000 over the concentration range

A low level phosphine standard (~0.42 ppb) was also prepared, to allow the detection limit (DL) to be calculated. Two different methods for DL calculation were used:

- i. Two times the signal to noise (S/N) of the phosphine peak in the low level standard based on "Peak to Peak" noise method, and
- ii. The standard deviation of the concentrations measured in seven replicate analyses of the low level standard.

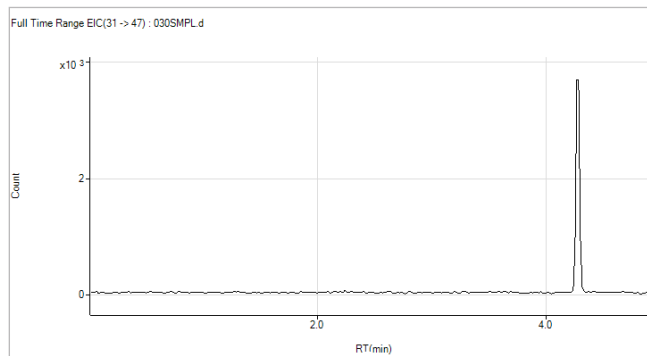


Figure 2. Chromatogram of 0.42 ppb PH₃ standard. S/N: 96.9

In the chromatogram shown in Figure 2, a S/N ratio of 96.9 was determined for the phosphine peak. Using the equation $DL = 2 \times ((\text{concentration of standard}) / (S/N))$, a detection limit approximation of 8.67 ppt was calculated based on $2 \times ((0.42 \text{ ppb}) / (96.9))$. Using the standard deviation method, where multiple replicates of the low level standard were analyzed, the detection limit was 19 ppt.

Multielement analysis of germane, arsine and phosphine

In order to check the performance of the method when measuring multiple masses within a single analysis, Ge, As and P were analyzed together and integration times were adjusted so as to not exceed the 1 second scan time limit. Ge and As were measured as their O₂ reaction product ions: GeO⁺ and AsO⁺, as was the case with P (PO⁺). The total integration time for all three mass pairs was 0.908 seconds, as shown in Table 3.

Table 3. Acquisition parameters for P, Ge and As

Element	Q1 -> Q2	Integration time/Mass (sec)
P	31 -> 47	0.5000
Ge	74 -> 90	0.2000
As	75 -> 91	0.2000

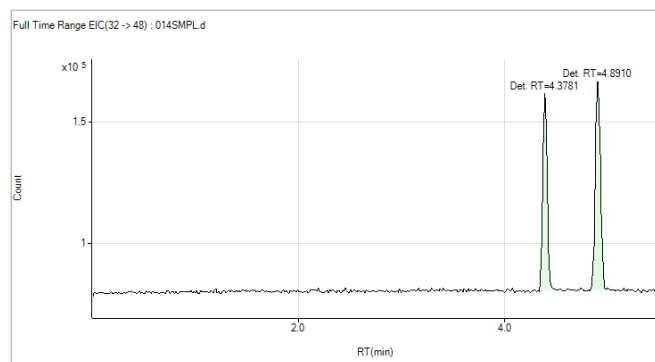
Linear multipoint calibration curves were generated from phosphine, germane and arsine standards at 4.1, 8.8 and 18.3 ppb. The detection limits for all three analytes, calculated from the S/N measured using the low level calibration standard, are shown in Table 4.

Table 4. GC-ICP-QQQ detection limits for P, Ge and As

	Calibration R value	S/N of 4.1 ppb standard	DL using S/N (ppb)
PH ₃	1.0000	671	0.012222
GeH ₄	1.0000	2111	0.00388
AsH ₃	1.0000	6373	0.00129

Analysis of hydrogen sulfide and carbonyl sulfide

Hydrogen sulfide (H₂S) and carbonyl sulfide (COS) were analyzed using O₂ mass-shift mode based on the ICP-QQQ measurement of sulfur as the ³²S¹⁶O⁺ reaction product ion at *m/z* 48. An integration time of 0.75 seconds was chosen and a calibration curve was generated from standards at 4.28, 7.49 and 17.04 ppb. A chromatogram of the 4.28 ppb standard is shown in Figure 3. A low level standard (~2.3 ppb) was also prepared, to allow the DL to be calculated. DLs for H₂S and COS, calculated from the S/N analysis of the 2.3 ppb standard and the analysis of 7 replicate measurements of the low standard, are shown in Table 5.

**Figure 3.** Chromatogram of 4.28 ppb standard of H₂S and COS**Table 5.** MDL calculations for H₂S and COS

	Calibration R value	S/N of 2.3 ppb standard	DL using average S/N (ppb)	DL based on 7 replicates (ppb)
H ₂ S	1.0000	46	0.10602	0.20506
COS	1.0000	44.8	0.1085	0.11893

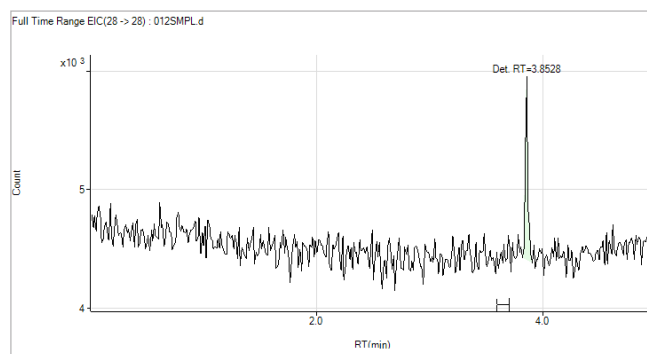
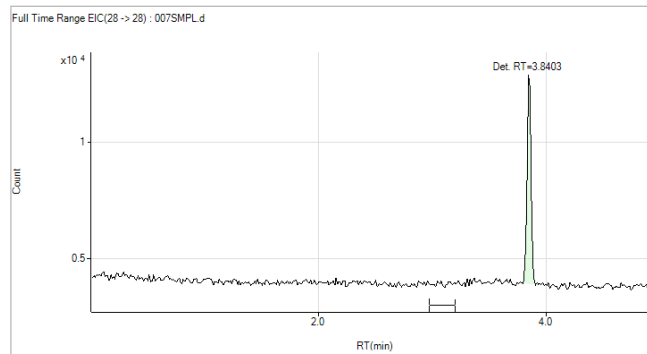
Analysis of silane

The primary polyatomic interferences on ²⁸Si⁺ are ¹²C¹⁶O⁺ and ¹⁴N₂⁺ due to the presence of CO₂, N₂, and O₂ in the argon supply and from air entrainment into the plasma. H₂ was selected as the reaction gas for Si analysis, as both the CO⁺ and N₂⁺ interferences react readily with H₂ cell gas. Si⁺ remains unreactive and so can be measured, free from interferences, at its original mass.

Data acquisition was performed using on-mass MS/MS mode with both Q1 and Q2 set to mass 28, and using an integration time of 0.75 seconds. A calibration curve for silane was prepared at 4.2, 7.8 and 18.1 ppb and an R value of 1.00 was achieved over this concentration range. MDLs for SiH₄ calculated from the S/N analysis of the 4.2 ppb standard and analysis of seven replicate measurements of the low standard are shown in Table 6.

Table 6. MDLs for silane based on 4.2 ppb standard

	Calibration R value	DL using average S/N (ppb)	DL based on 7 replicates (ppb)
SiH ₄	1.0000	0.196764	0.141877

**Figure 4.** Chromatogram of 4.2 ppb silane standard (upper) and ~0.4 ppb silane (lower)

It should be noted that the elevated background at mass 28 in the silane chromatograms shown in Figure 4 is most likely due to column bleed from the thick film DB-1 column (methyl silicone stationary phase) used in these experiments. This Si background signal might be reduced by using a porous polymer type column.

Comparison of GC-ICP-QQQ and GC-ICP-MS DLs

For comparison purposes, H₂S, COS, PH₃, GeH₄, AsH₃, and SiH₄ were analyzed by both GC-ICP-QQQ with the 8800 ICP-QQQ, and GC-ICP-MS using the same GC method with an Agilent 7900 conventional quadrupole ICP-MS. A summary of the detection limits (DLs) for both techniques is given in Table 7. For analytes where the background noise is very low (Ge-74, As-75), single digit ppt level detection limits are easily achieved using either GC-ICP-MS or GC-ICP-QQQ. However, for analytes that are prone to higher backgrounds (P-31 and S-32), significantly lower detection limits can be achieved using MS/MS with O₂ cell gas and measuring the oxygen addition reaction product ions PO⁺ and SO⁺ in mass-shift mode. In addition, MS/MS mode with H₂ cell gas provides effective removal of background interferences at mass 28, allowing on-mass measurement of Si at its primary isotope.

Conclusions

The significantly lower background and higher sensitivity of the Agilent 8800 ICP-QQQ resulted in a GC-ICP-QQQ method that shows a clear advantage for the determination of a range of contaminants in high purity gases at the low detection levels demanded by the industry. Compared to GC-ICP-MS with conventional quadrupole ICP-MS, GC-ICP-QQQ DLs for silane, phosphine, hydrogen sulfide, and carbonyl sulfide were lower by a factor of 5 to 10, with silane detection limits in the ~200 ppt range and phosphine detection limits in the ~15 ppt range.

More Information

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Table 7. Detection limit comparison between GC-ICP-QQQ and GC-ICP-MS

Hydride gas	8800 ICP-QQQ		7900 ICP-MS	
		DL, ppb		DL, ppb
H ₂ S	32->48 (O₂)		32 (No gas)	
	MDL 7 reps	0.21	MDL 7 reps	0.62
	MDL 2 x S/N	0.11	MDL 2 x S/N	0.22
COS	32->48 (O₂)		32 (No gas)	
	MDL 7 reps	0.12	MDL 7 reps	0.51
	MDL 2 x S/N	0.11	MDL 2 x S/N	0.21
PH ₃	31->47 (O₂)		31 (No gas)	
	MDL 7 reps	0.019	MDL 7 reps	0.139
	MDL 2 x S/N	0.009	MDL 2 x S/N	0.077
GeH ₄	74->90 (O₂)		74 (No gas)	
	MDL 7 reps	NA	MDL 7 reps	0.013
	MDL 2 x S/N	0.0038	MDL 2 x S/N	0.0013
AsH ₃	75->91 (O₂)		75 (No gas)	
	MDL 7 reps	NA	MDL 7 reps	0.016
	MDL 2 x S/N	0.0013	MDL 2 x S/N	0.006
SiH ₄	28->28 (H₂)		28 (H₂)	
	MDL 7 reps	0.14	MDL 7 reps	1.09
	MDL 2 x S/N	0.196	MDL 2 x S/N	1.18

NA = not available

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