

Gas chromatographic separation of metal carbonyls in carbon monoxide with detection using the Agilent 8800 ICP-QQQ

Application note

Petrochemical, semiconductor

Authors

William M. Geiger, Blake McElmurry
and Jesus Anguiano
CONSCI, Ltd., Pasadena, Texas, USA



Introduction

Carbon monoxide (CO) gas is used in a number of industries and applications. For example, the semiconductor industry uses it to moderate the etch rate of silicon wafers and improve selectivity for greater control of the process. In pharmacology, CO has been used therapeutically to mitigate organ rejection in transplant patients. It can also be a major constituent in cogeneration gas or syngas. However, CO can form a metal carbonyl on contact with various metals including chromium, molybdenum, iron, nickel, cobalt, and several more. Iron carbonyl [$\text{Fe}(\text{CO})_5$] and nickel carbonyl [$\text{Ni}(\text{CO})_4$] are the most common examples [1].

Metal carbonyls are highly toxic and the therapeutic use of carbon monoxide can lead to exposure to carbonyls that may be more harmful than the CO itself. In the etching process, if a metallic carbonyl residue forms on the surface of the wafer, it can cause electronic device failure. Similarly, if CO is present at high levels in syngas, the deposition of carbonyls on gas turbine fan blades may lead to the catastrophic failure of the turbine. Because of the potential harm caused by metal carbonyls, it is important that the



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concentration of metal carbonyls in CO used in mixed gases is known or controlled before the gas is used.

Gas chromatography with electron capture detection (ECD) can be used for the analysis of nickel and iron carbonyl, with excellent sensitivity [2]. However, the method requires a laborious and complicated calibration strategy that can lead to poor accuracy due to errors introduced during sample handling and analysis. A novel approach using a GC coupled to a triple quadrupole ICP-MS (ICP-QQQ) operating in MS/MS mode offers an efficient and elegant alternative approach for the analysis of Ni, Fe and other metal carbonyls.

There are several challenges that need to be addressed for GC-ICP-QQQ analysis to be successful. Since metal carbonyl gas standards are not readily available, a calibration strategy must be developed. As both nickel and iron carbonyls can easily form or deposit on steel surfaces in a carbon monoxide matrix, a chromatographic system without metal in the flow path must be used to avoid erroneous measurements. Finally, for optimum performance, two tune conditions are required for the ICP-QQQ as the best performance for nickel is achieved using helium gas in the ORS collision/reaction cell, while performance for iron is superior with hydrogen cell gas.

Experimental

Instrumentation

An Agilent 7890B Gas Chromatograph was coupled to an Agilent 8800 Triple Quadrupole ICP-MS, using a combined gas/liquid introduction interface, as illustrated in Figure 1.

All sample wetted parts were composed of PEEK, including tubing, sampling lines, and a Valco 10 port gas sampling valve (GSV). The GSV was used to introduce two gas volumes to the GC column (Figure 2). A sample loop of 280 μL was used for the introduction of the calibration standard or carbon monoxide sample, and a standard addition loop of 70 μL was used as an internal calibration/check standard.

The combination GC-ICP-QQQ interface (with both GC effluent connection and conventional nebulizer/spray chamber) enabled the liquid standard solution or blank (introduced via the nebulizer) to be mixed with the gaseous effluent from the GC, before being passed to the plasma torch [3]. GC operating conditions are given in Table 1.

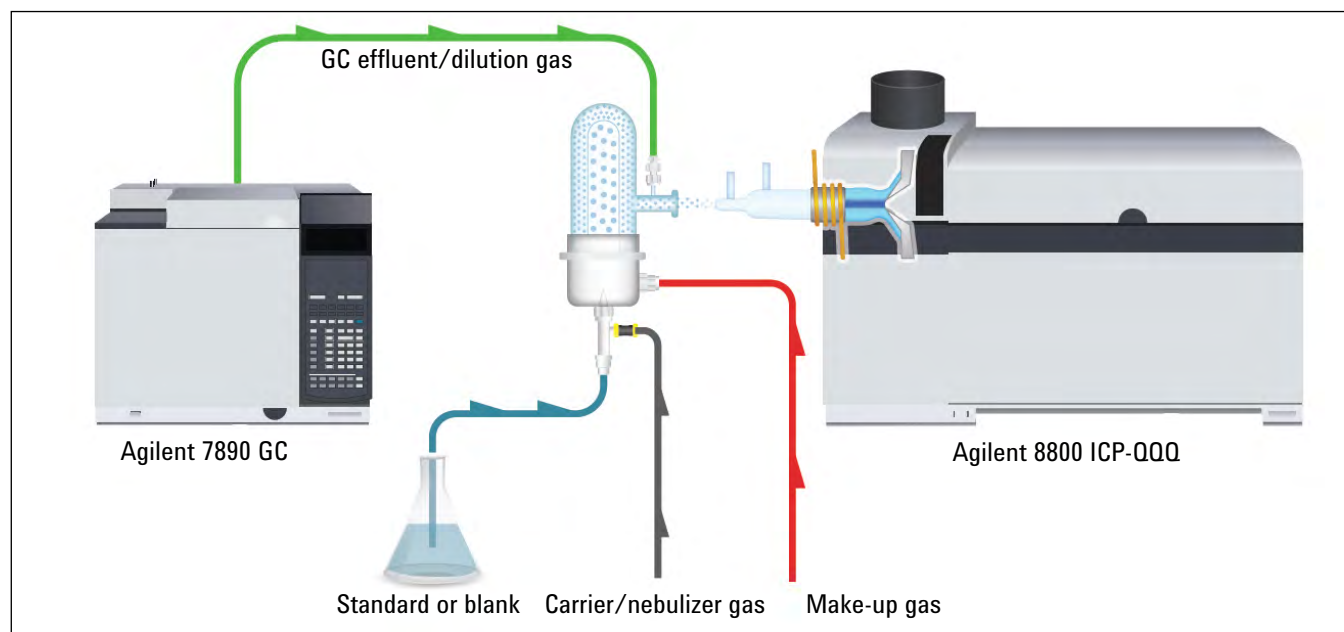


Figure 1. GC-ICP-QQQ interface for the simultaneous aspiration of liquid standard or blank and GC effluent

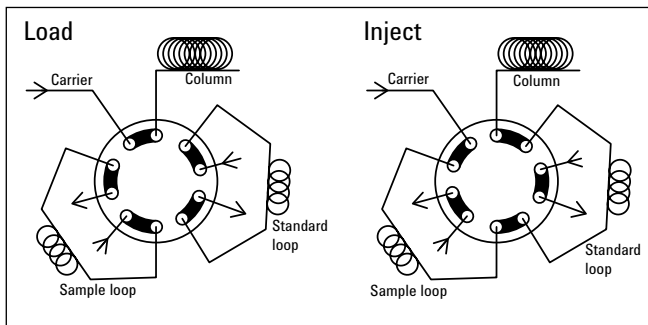


Figure 2. Valco 10 port PEEK gas sampling valve (GSV) flow path providing standard addition capability

Table 1. Agilent 7890 GC conditions

Carrier	Helium @ 13 psig
Column	30 m x 0.53 mm x 1.5 μm DB-5
Oven	40 °C Isothermal
Sample size	280 μL

Acquisition conditions

In this study, the 8800 ICP-QQQ was operated in MS/MS mode using helium as the collision gas for the on-mass measurement of Ni at m/z 58 (integration time 0.1 seconds/mass). Hydrogen cell gas mode was used for the on-mass measurement of Fe at m/z 56 (integration time 0.5 seconds/mass). Tuning conditions were almost identical for the two modes, the only differences were in the KED voltage and the cell gas flow. Bromine was determined in He mode at m/z 79 (integration time 0.1 seconds/mass).

Table 2. Agilent 8800 ICP-QQQ operating conditions

	He mode	H ₂ mode
RF power (W)	1550	
Sample depth (mm)	8.0	
Dilution gas flow (L/min)	0.2	
Extract 1 (V)	0.0	
Extract 2 (V)	-165.0	-160.0
Kinetic Energy Discrimination (V)	3.0	0.0
Cell gas flow (mL/min)	3.30	7.00
Integration time/mass (seconds)	Ni, Br: 0.1	Fe: 0.5

Calibration

Calibration was performed by the aspiration of aqueous standards (Inorganic Ventures, Christiansburg, Virginia, USA, standard IV-ICPMS-71A) of nickel (0.17 μmoles/L), iron (0.18 μmoles/L), and a bromine standard (12.8 μmoles/L). This allowed the relative response of Ni and Fe to Br to be determined, as illustrated for Ni in Figure 3. In order to determine nickel or iron carbonyl concentrations, a gas standard of methyl bromide (101 ppb) was introduced to the GC via the GSV. Relative response factors were used to quantitate for the unknowns as illustrated in Figure 4 [4]. The methyl bromide gas phase standard was prepared at 101 ppb by dynamically diluting a higher level standard (certified as 9.90 ppm NIST traceable, sourced from United Specialty Gases, Houston, Texas, USA).

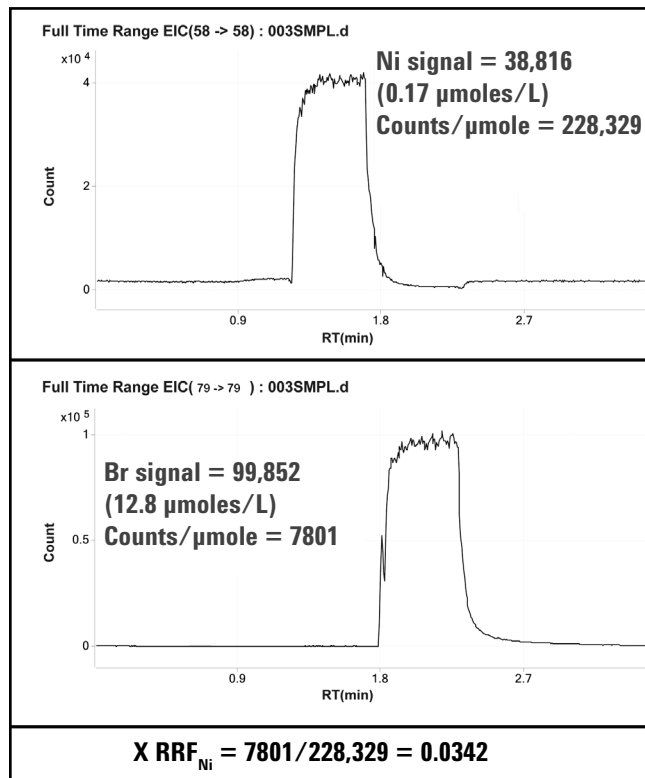


Figure 3. Calculation of relative response factor (RRF) for Ni, from aspiration of aqueous nickel and bromine standards

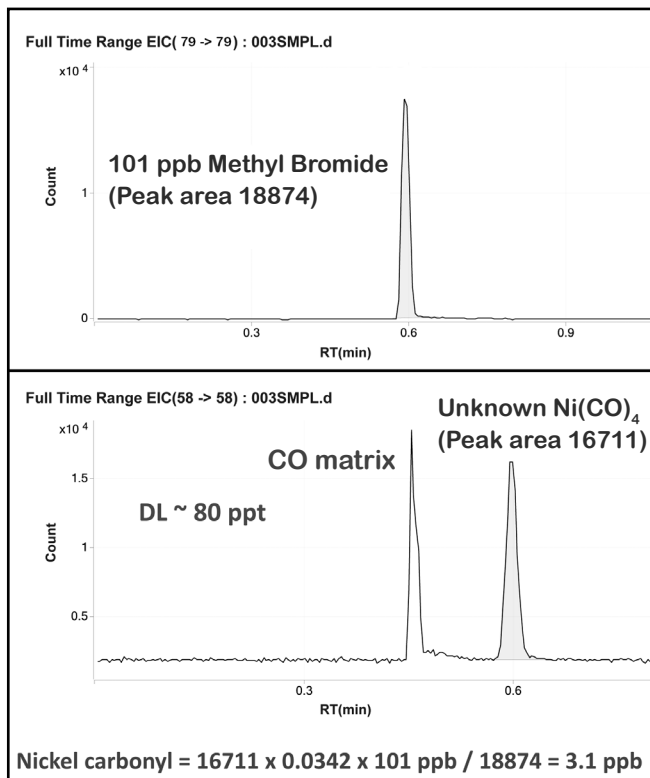


Figure 4. Analysis of known gas phase bromine standard as a surrogate standard for the determination of unknown nickel carbonyl

The ICP-MS MassHunter software allows multiple tune conditions to be applied in series during a single time resolved analysis (TRA) acquisition. Mode switching allows the acquisition mass and cell mode to be changed mid-run, so nickel and iron can be measured under optimum conditions (using helium and hydrogen cell gas, respectively), in the same analytical run. As there is a reasonable interval between the elution of nickel carbonyl and iron carbonyl, there is sufficient time for switching tune conditions so that both elements can be measured from a single injection. Since two tune modes were used in the analysis (He mode for Ni and Br, and H₂ mode for Fe) there was a virtual gain in sensitivity when switching mode since only one mass was monitored at a time allowing for better signal averaging. This is illustrated in Figure 5.

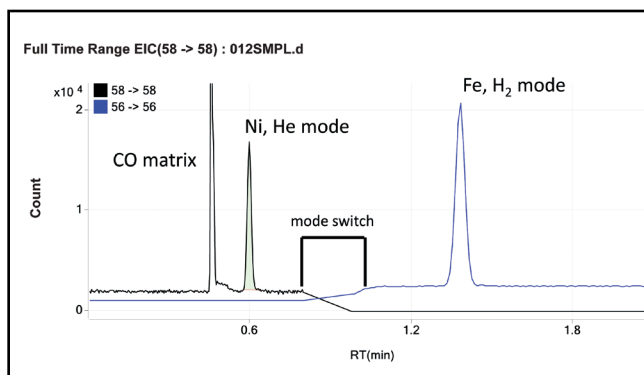


Figure 5. Tune mode switching for optimum measurement conditions during TRA acquisition

Limits of Detection

The detection limit (DL) for nickel carbonyl was estimated to be 80 ppt based on 2x signal-to-noise (S/N). Since the iron carbonyl peak is broader, the integration time was increased from 0.1 to 0.5 seconds/mass in the second tune so that the S/N ratio was improved. For comparison purposes, two different methods were used to establish the DL for iron carbonyl. A simple 2 x S/N calculation gave a DL of ~70 ppt. Applying a t-test to eight replicate analyses resulted in a more statistically valid value of 140 ppt. The nickel DL was improved at least twofold using He gas mode compared to no gas. Similarly, the DL for iron was improved about three fold using hydrogen versus helium as the cell gas.

An important matter in achieving very low detection limits, particularly for iron carbonyl, is the cleanliness of the blank solution. Figure 6 shows the signal plot for a suspect blank compared to a five level calibration. Note that the suspect blank is over 2 ppb on a weight basis, which would raise the noise level and therefore the detection limit for the gas phase analysis.

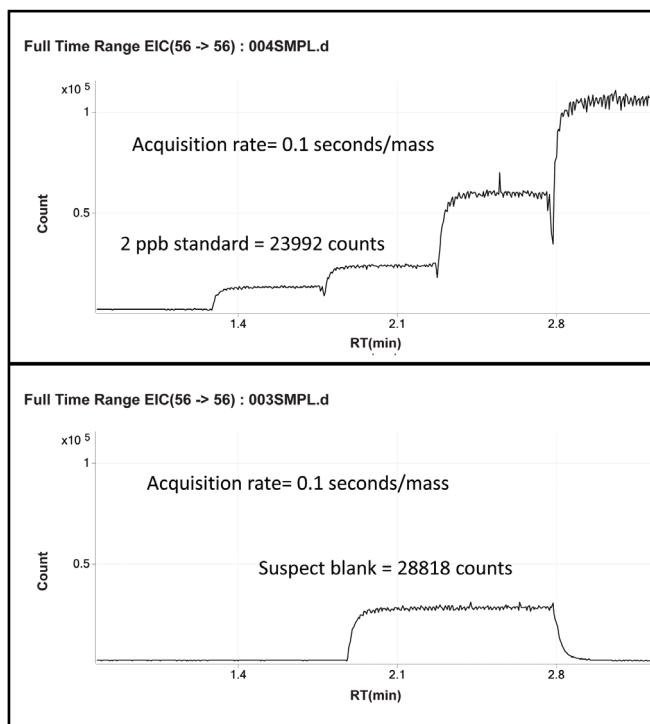


Figure 6. Aqueous standards (top) versus contaminated blank (bottom)

Conclusions

The Agilent 8800 ICP-QQQ's ability to use multiple tune conditions in a single chromatographic analysis makes it possible to use optimum acquisition settings for each analyte. This enables the GC-ICP-QQQ to achieve excellent detection limits for nickel carbonyl and iron carbonyl, two of the most analytically challenging contaminants in carbon monoxide. The detection levels of 70-80 ppt are comparable to GC-ECD detection and are well below what is currently required by the various industries. However, the multi-element capability of ICP-QQQ ensures that other metal carbonyls can also be successfully measured with this method, including $\text{Co}_2(\text{CO})_8$, $\text{Cr}(\text{CO})_6$, $\text{Mo}(\text{CO})_6$, and $\text{Fe}_2(\text{CO})_9$.

The GC was interfaced to the ICP-QQQ via a second inlet connection to the standard ICP spray chamber, to allow simultaneous aspiration of an aqueous standard. This approach is essential to performing quantitative measurements of carbonyl species, for which gas phase standards are not typically available. The simultaneous aspiration of an aqueous standard also provides sufficient oxygen to prevent carbon buildup on the torch or cones from the carbon monoxide, avoiding the need to add additional oxygen.

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