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Mass spectrometry

Reaching sub-ppm limits of detection for carbon, nitrogen and oxygen with the Element GD Plus GD-MS

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Introduction

Manufacturers of semiconductor materials and high purity metals use a number of different analytical techniques to assess the purity of the materials that they produce. Glow discharge mass spectrometry (GD-MS) is a popular tool for analyzing a wide range of metallic and non-metallic impurities. However, the quantification of gas phase elements like trace carbon, nitrogen and oxygen within materials has traditionally been accomplished through combustion techniques, requiring a second analytical instrument.

The fast flow source of the Thermo Scientific™ Element™ GD Plus GD Mass Spectrometer is well suited for analyzing gas phase elements like C, N and O. This is because the high discharge gas flow can rapidly remove water, carbon dioxide, nitrogen and oxygen which could be adsorbed on surfaces. However, achieving low detection limits for carbon, nitrogen and oxygen requires a sufficiently clean argon discharge gas.

In this technical note, we introduce the CNO option for the Element GD Plus GD-MS. The CNO option cleans the argon discharge gas through purification units adsorbing moisture, carbon dioxide and nitrogen traces from the argon gas supplied. This allows sub-ppm limits of detection to be achieved for carbon, nitrogen and oxygen.

What is the CNO option?

The CNO option of the Element GD Plus GD-MS provides the tools to analyze ppm and sub-ppm levels of atmospheric gas elements in samples. The fast-flow source of the Element GD Plus GD-MS is uniquely suited for the analysis of gas phase elements. The high discharge gas flow removes atmospheric contaminants, mainly H_2O and CO_2, and N_2 and O_2 that have been adsorbed onto the surfaces. The CNO option cleans the incoming discharge gas, allowing low levels of detection for carbon, nitrogen and oxygen.

The CNO option offers an alternative gas line for the discharge argon gas (Figure 1). Argon gas is led to the source through a moisture trap and a gas purifier before entering the instrument via a mechanical valve. This is used when low carbon, nitrogen and oxygen backgrounds are required. The CNO option consists of four key components (Figure 1, blue line):

- Moisture trap: which acts as a pre-filter for C (CO_2) and O (H_2O)
- Heated gas purifier: which traps C, N and O
- Mechanically adjustable valve: high purity valve to regulate the flow of purified argon
- High purity, high quality steel capillaries: avoiding any polymer sealings and keeping the number of connections to a minimum

Determining the limits of detection for CNO

The Limits of Detection (LoD) for carbon, nitrogen and oxygen were determined here through repeat measurements of a high purity copper sample with low carbon, nitrogen and oxygen content, using the CNO option. 90 seconds fast pre-sputtering at 60 mA in DC mode was applied after sample change (1 min) and source pump down (1 min). C, N and O levels stabilized within a period of 40 – 60 min, after which the measurement was made. Instrument set-up conditions are listed in Table 1.

The calibration lines of C, N and O were determined through the analysis of a number of certified reference materials (Figure 2).

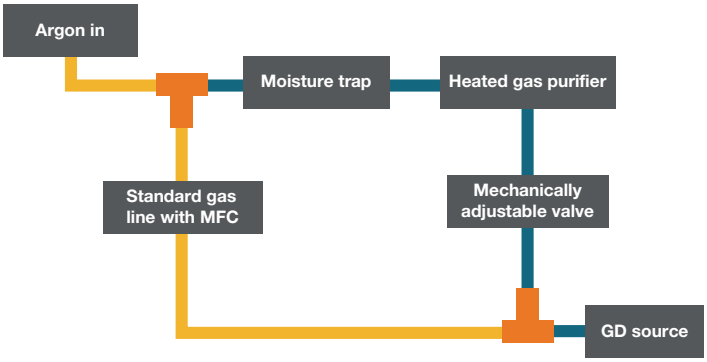

Figure 1. Schematic of the alternative gas line (blue) offered by the CNO option.

Table 1. Instrument set-up conditions for determining LoDs for carbon, nitrogen and oxygen

Discharge Voltage (V)	1000
Discharge Current (mA)	≈ 13
Mode	Pulsed/Modulated DC
Pulse Frequency (kHz)	2
Pulse duration (µs)	75
Source vacuum (mbar)	1.06
Discharge gas (mL/min)	≈ 500
Resolution	4000
Matrix sensitivity	≈ 1.5 x 10^{10} cps (^{63}Cu + ^{65}Cu at 4000 Resolution), equivalent to ≈ 2.5 nA ≈ 1.3 x 10^{10} cps (^{56}Fe), equivalent to ≈ 2 nA

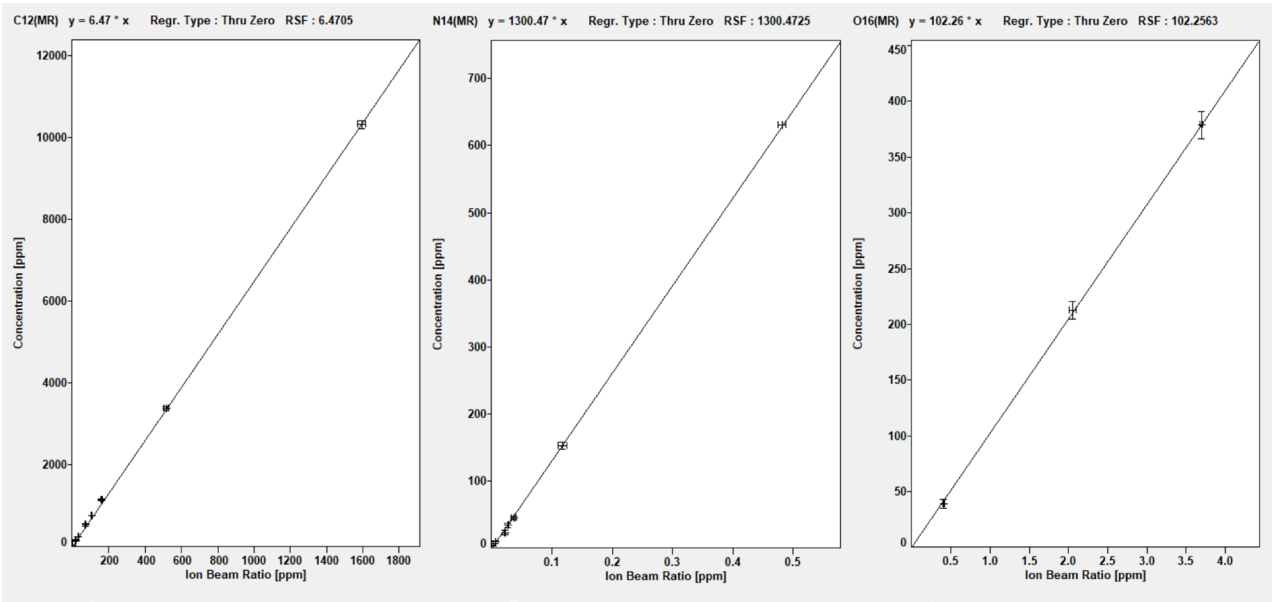

Figure 2. Calibration line of (A) carbon, (B) nitrogen, and (C) oxygen. Note that the carbon and nitrogen calibrations used iron-based certified reference materials, whereas the oxygen calibration was generated using copper-based certified reference materials. The lowest calibration point was 5.1 ppm, 2.4 ppm and 38 ppm for C, N and O respectively. Calibration line of C in Fe matrix using ECRM 098-1, ECRM 379-1, SRM 1766, ECRM 297-1, SRM 1767, ECRM 270-1, ECRM 096-1, SRM 1762, and SRM 1761. Calibration line of N in Fe matrix using ECRM 098-1, SRM 1767, SRM 1762, SRM 1766, SRM 1761, ECRM 297-1, and JK 27-A. Calibration line of O in Cu matrix using BAM-379/1, BAM-379/2, and BAM-379/3.

The slopes of the calibration lines are the Relative Sensitivity Factors (RSF) in the corresponding matrix. In iron matrix, the RSF factors are called Standard RSF (sRSF) values.

$$RSF\ (x\ in\ Cu) = sRSF\ (x\ in\ Fe) / sRSF\ (Cu\ in\ Fe)$$

The slope of the Cu calibration line in Fe matrix was 3.18. The resulting RSF values in Cu matrix are displayed in Table 2.

Table 2. RSF values in Cu matrix in pulsed mode. The asterisk (*) indicates a derived value using the above equation.

	C	N	O
RSF in Cu matrix	2.03*	409*	102

The Ion Beam Ratios (IBR) of 3 consecutive analyses (3 x 4 min for a suite of 77 elements including C, N, O) are shown in Table 3. The average of these values is the IBR Background Equivalent Concentration (BEC). The IBR Limits of Detection (LoD) are calculated as 3 times the standard deviation of the individual analysis. The Mass Fraction of each element is determined from the IBR multiplied by the RSF value for the element in that particular matrix.

Table 3. BEC and LoD for carbon, nitrogen and oxygen. ^{12}C, ^{14}N and ^{16}O expressed as Ion Beam Ratios and the corresponding mass fractions.

	^{12}C (MR)	^{14}N(MR)	^{16}O(MR)
Repeat 1 [ppm IBR]	0.19	0.0009	0.075
Repeat 2 [ppm IBR]	0.18	0.0008	0.073
Repeat 3 [ppm IBR]	0.18	0.0010	0.072
BEC [ppm IBR]	0.18	0.0009	0.073
LoD (3x SD) [ppm IBR]	0.02	0.0003	0.005
BEC [ppm Mass Fraction]	**0.4**	**0.4**	**8**
LoD [ppm Mass Fraction]	**0.05**	**0.12**	**0.5**

The results show that all 3 elements can be analyzed at sub-ppm levels. The Mass Fraction BECs in the copper sample analyzed are 0.4 ppm for C and N, and 8 ppm for O. Mass Fraction LoDs for all 3 elements are in the ppb range.

What are the other advantages of the Element GD Plus GD-MS?

The Element GD Plus GD-MS has a unique fast flow source design that has several major advantages over static GD sources, such as:

- Rapid sample pumping times
- Easy sample handling and analysis
- High sensitivity
- High signal-to-noise ratio
- Less polyatomic interferences
- Low abundance sensitivity

The fast-flow source dramatically improves sample throughput, with rapid pumping down of the sample (< 1 min) for fast sample analysis. Coupled with this, the unique source design enables samples to be easily exchanged (< 2 min for many applications), significantly improving your lab productivity and decreasing the cost of analysis.

The fast flow design also results in outstanding signal-to-noise ratios, enabling sub-ppb limits of detection for most analytes. Furthermore, there is a factor 10 reduction in polyatomic interferences relative to static GD sources, and abundance sensitivities of < 15 ppb (1 amu on ^{63}Cu, medium resolution) can be routinely achieved. This makes the Element GD Plus GD-MS ideally suited to analysis of ultra-high purity materials.

With the Element GD Plus GD-MS there is no requirement for liquid nitrogen to achieve the source vacuum required for analysis. This makes analysis simpler and has the added benefit that it allows the analysis of a wider range of samples, including porous materials, like graphite, which would adsorb water and CO_2 in the presence of liquid nitrogen.

Conclusion

We have demonstrated how the CNO option for the Element GD Plus GD-MS increases its versatility, allowing trace amounts of carbon, nitrogen and oxygen to be quantified simultaneously with a wide range of metallic and non-metallic impurities. The low LoDs for carbon (0.05 ppm), nitrogen (0.12 ppm) and oxygen (0.5 ppm) enable a wide range of samples to be screened for impurities. Coupled with the fast analysis times and sample loading times, the CNO option makes the Element GD Plus GD-MS the instrument of choice for trace elemental analysis of semiconductor materials and high purity metals.

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