Trace Analysis of Gas Phase Elements in Metals by Fast-Flow GD-MS

Joachim Hinrichs, Shona McSheehy Ducos
Thermo Fisher Scientific, Bremen, Germany

Overview

Purpose: Improve the detection limits (LODs) and Background Equivalent Concentrations (BECs) of the gas phase elements Carbon, Nitrogen, and Oxygen (C, N, O) on the Thermo Scientific™ ELEMENT™ GD PLUS GD-MS.

Methods: Several high purity Copper samples and reference materials were analyzed for low levels of C, N, O. A heated source was developed to improve the release of adsorbed gases in the glow discharge cell. Gas purification options were tested to verify the importance of discharge gas purity.

Results: Carbon BECs of <1ppm in Copper samples, expressed as uncalibrated Ion Beam Ratios, were achieved. Large improvements in LODs and BECs were observed for Nitrogen and Oxygen, although for these elements the calibration factors will need to be verified. Preliminary results indicate detection limits in the range 1 – 10 ppm.

Introduction.

The ELEMENT GD PLUS high-resolution glow-discharge mass spectrometer (GD-MS) features a fast-flow source enabling a much higher sample turn-around than the previously used static high-vacuum sources that required intense cooling with liquid nitrogen. While the fast-flow concept is generally superior in sensitivity, speed, analytical performance and formation rate of polyatomic interferences, it suffers from elevated backgrounds of the gas phase elements Carbon, Nitrogen, and Oxygen.

The goal of this study was to identify the contamination sources and to find an instrumental solution for sub-ppm analysis of the gas phase elements.

Methods

Sample Preparation

The certified reference materials ERM 366 and BS14500 were used for this study. Several samples of 99.9999% purity were analyzed as unknowns for test purposes. The sample surface was prepared by either lathing, grinding on SiC paper, or by grinding followed by acid etching.

Test method

The Copper samples were run using the ELEMENT GD PLUS GD-MS in DC mode, using Medium Mass resolution (MR, R>4000).

Data Analysis

All analytical signals counted by the detection system as counts per second (cps) were normalized to the Copper matrix signal. This result is the Ion Beam Ratio (IBR), representing an uncalibrated ion ratio. As a second step, the IBR acquired were recalculated based on the instrument's semi-quantitative Standard RSF table to achieve semi-quantitative results. While this table contains a calibration factor for Carbon, no calibration information is available for Nitrogen and Oxygen.

Thermo
SCIENTIFIC

Results

Sample surface contamination

The samples were analyzed using continuous DC mode at 40 mA discharge current, using a presputter time of ~30-40 min followed by data acquisition. The anode cap and flow tube were made from Tantalum, the anode and cone from Stainless steel. The long pre-sputter time is partly due to surface contamination from either atmospherically adsorbed or grinding contamination deeper in the material.

As an example of the contribution to carbon BEC from SiC grinding, Fig. 1 shows the pre-sputter behavior as a function of time. Each point represents the average of 3 minutes data acquisition. The distinct drop of the Carbon level is from the transition form the SiC contaminated grinding zone to the non-contaminated zone underneath, where stable and low Carbon levels are observed.

FIGURE 1. Input of Carbon background from the SiC grinding step and incomplete acid leaching. Vertical scale shows semi-quantitative concentrations in ng/g.

FIGURE 2. Carbon and Oxygen signal before (top) and after installation of moisture trap in the gas line (bottom).

Gas purity

The quality of the Argon used as a discharge gas is of crucial importance for CNO analysis. It is difficult to differentiate between overall gas purity vs. contamination in the gas distribution. Therefore, for the experiments, the 4N8 Argon from the in-house distribution was coupled directly with the GD source, minimizing the connections in the gas distribution. With this setup, various gas purification units were installed in-line to evaluate the efficiency of gas purification on the analytical BEC levels of CNO.

A moisture trap was particularly effective and has shown the most significant drop in BEC, especially for Oxygen content due to capturing residual water. The carbon BEC level was also significantly reduced (Figure 2).

Adsorption

During sample change, the Glow Discharge chamber is exposed to atmospheric gases, that are assumed to adsorb in the glow discharge area. During measurement, these molecules are then desorbed, probably due to temperature effects and ion bombardment. The typical high initial CNO signal during pre-sputter time, and the long and slow decrease of the signal favors this hypothesis.

Procedure for optimized BEC for CNO:

- Heating out the anode area during and after sample change
- Counter stream of purge gas flow during sample change
- Extended pump down times to enhance desorption of loosely attached molecules
- Long pre-sputter times to coat the inner surface with freshly sputtered Cu material

FIGURE 3. Adsorption reduction by heating of the glow discharge source
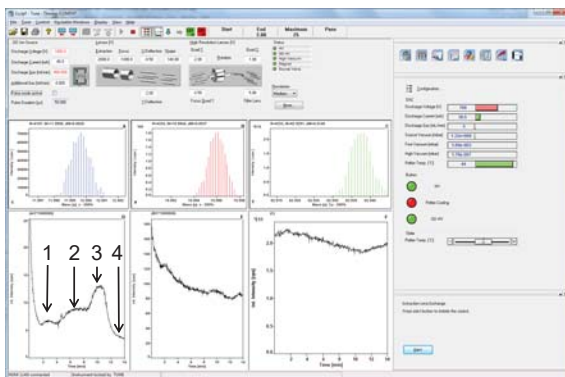
Heating steps:

1) Heater 45W
2) Water supply 50°C
3) Heater 65W
4) Heater off, water supply 18°C

Results

Based on IBR, the BEC achieved during these studies were <1ppm for C, N, O. Lowest values achieved were 0.25ppm C, 0.015ppm N, 0.008ppm O.

The lowest BEC yields 0.65ppm as a semi-quantitative concentration for Carbon. For O, a tentative calibration resulted in an RSF of ~90 for O in Cu. This would give a tentative O value for the lowest readings of ~1.7ppm. For Nitrogen, no calibration estimate can be given. Presumably, the RSF will be similar to Oxygen, thus yielding a single digit ppm BEC for N.

Conclusion

- The ELEMENT GD PLUS GD-MS can detect sub-ppm levels of the gas phase analytes Carbon, Nitrogen, and Oxygen.
- Adsorbed gas molecules and overall gas purity show the largest input on the CNO backgrounds.
- Analysis duration is ~45 minutes.
- Findings will be implemented into instrumental setup.

Thermo
SCIENTIFIC

A Thermo Fisher Scientific Brand