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APPLICATION NOTE 30237

# GD-MS analysis of sulphur at the ultra-trace level


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**Keywords**
Element GD Plus, GD-MS, Nickel alloy, Sulphur, Ultra-trace


## Overview

The Thermo Scientific™ Element™ GD Plus high-resolution glow discharge mass spectrometer has been used to analyze ultra-trace concentrations of sulphur directly in solid Ni alloy samples.

## Methods

Accurate determination of sulphur in nickel alloys is of particular importance, since even sub-ppm levels may affect the properties of these materials, especially the high temperature oxidation resistance of aircraft engine blades. At such low concentrations, traditional combustion techniques for sulphur determination cannot be readily applied. Therefore, a reliable analytical technique is required for quality control of the production process and the final products.

This application report summarizes the results obtained on a series of Ni alloy materials of low sulphur content.

### Sample material and preparation

The samples analyzed for this report were a series of Ni alloy samples with expected sulphur concentrations in the single digit ppm to sub-ppm range. Prior to analysis, the sample surface was prepared by wet grinding using grit 80 SiC paper, followed by a finish with grit 120.

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## Instrumental settings

For analysis, optimum instrumental settings were established for sensitivity and signal stability as well as a reasonable analysis time. Instrumental settings are summarized in Table 1. While the primary focus of this analysis was to achieve accurate and precise analysis of low level sulphur, a multi Element analysis was performed in the same run. A pre-sputter time of 12 min was used to fully remove all surface contaminations, followed by an acquisition time of 8 minutes.

**Table 1. Instrument conditions.**

| | |
|---|---|
| Discharge current | 45 mA |
| Discharge voltage | ~ 800 V |
| Discharge gas (Ar) | 450 mL/min |
| Actual sensitivity | $4 \times 10^{10}$ counts per second (sum of matrix elements, Medium Resolution) |
| Anode material | Steel |
| Anode cap | Graphite |
| Flow tube | Graphite |
| Cone | Graphite |

As part of the method development, the mass separation of the $^{32}S$ peak from any interfering $^{16}O_2$ has been verified. The final analytical method measures only the $^{32}S$ peak, as shown in Figure 1 for the lowest level sample.

## Evaluation strategy

The evaluation used was based on measuring the intensities of selected isotopes which are then corrected for their isotopic abundance and calculated as Ion Beam Ratios (IBR). The ratios of analyte to matrix are then transferred into concentrations using Relative Sensitivity Factors (RSF) determined for the respective matrix and the Elements of interest. Calibration by GD-MS is typically carried out with reliable reference materials in the ppm range. Due to the known linear behavior of the detection system, especially the SEM (Secondary Electron Multiplier) used for determining low level count rates, the obtained RSF for calibration can be extended down to the ppb level.

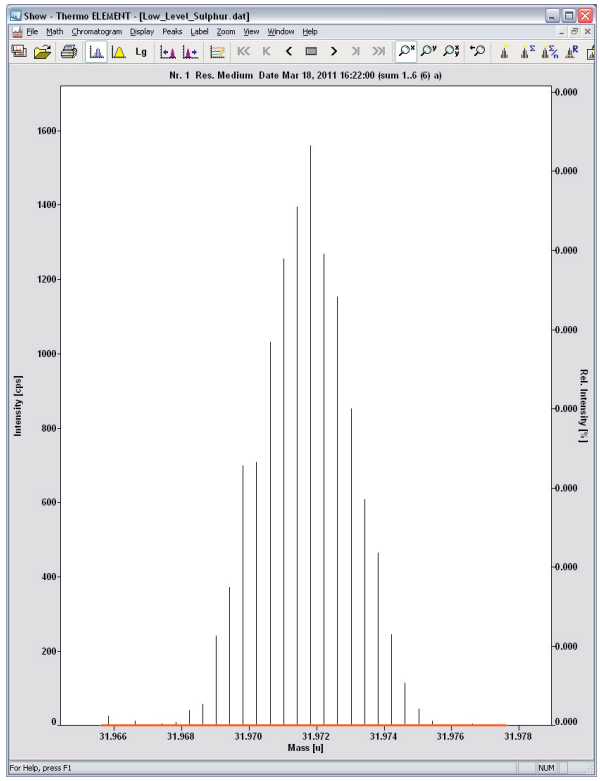


**Figure 1. Sulphur peak for Sample 1, analyzed in Medium Resolution ($^{32}S$, MR, R = 4,000); integration time per channel: 0.05 seconds.**

## Results and discussion

Table 2 shows the sulphur results of the three samples analyzed. Each sample was run on three different days. Prior to each analysis, the sample surface was freshly prepared.

On the first day of analysis, a single point calibration with the Standard Reference Material NIST 1249 was carried out, and was then applied to all following sample analyses. This standard is a nickel based super alloy (Inco 718) and was chosen because it resembles the sample compositions quite closely. Secondly, the sulphur content of this SRM is at a similar low level as the samples, with a sulphur reference value of 6.4 ± 1 ppm.

Table 2. Calibrated with NIST 1249: 6.4 ± 1.0 ppm Sulfur certified.

| Sulfur concentration [ppm] | | | | | | |
|---|---|---|---|---|---|---|
| Spot | 1 | 2 | 3 | AVG | STD | RSD |
| Date | Mar 04 | Mar 18 | Mar 22 | n = 3 spots | n = 3 spots | n = .3 spots |
| Sample 1 | 0.060 | 0.058 | 0.065 | 0.061 | 0.003 | 5.7% |
| Sample 2 | 0.348 | 0.343 | 0.355 | 0.35 | 0.01 | 1.7% |
| Sample 3 | 4.03 | 3.93 | 3.90 | 4.0 | 0.1 | 1.7% |

During this study, it was determined that significant amounts of sulphur originated from the stainless steel tubing material used for both, the in-house argon supply and the connection to the mass spectrometer. Therefore, a gas purification kit (PN #1306710) was developed for reducing the background contribution of sulphur introduced into the glow discharge cell. In addition to a gas purification cartridge, specially coated gas transfer capillaries were used upstream to the source.

These improvements have now been implemented in the standard Element GD Plus mass spectrometer configuration, and can also be retrofitted for installed instruments, thus facilitating low level sulphur analyses.

## Conclusions

The Thermo Scientific Element GD Plus high-resolution glow discharge mass spectrometer enables the precise determination of sulphur at trace levels. In nickel alloy samples with sulphur concentrations on the order of several hundreds of ppb, an excellent repeatability of 2% RSD was achieved on a day-to-day basis; double digit ppb levels can be quantified with a repeatability of 6% RSD.


## Acknowledgements

We thank Pratt & Whitney, East Hartford, CT, USA for providing the low level samples used for this report.


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