

Gallium Analysis Using μ s-Pulsed Fast Flow Glow Discharge Mass Spectrometry

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ABSTRACT

Sector field μ s-pulsed Fast Flow Glow Discharge mass spectrometry (μ s-FF-GD-MS) is routinely applied for the direct analysis of a wide range of materials. Especially for aerospace, electronics and photovoltaic industries, quality control at high sample turnaround is required, for example for nickel super alloys producers or high purity copper refineries.

The Thermo Scientific™ Element GD™ Plus GD-MS features a fast flow glow discharge source that can be operated in continuous or pulsed mode. For most metals, including indium and tin with rather low melting points, no special requirements for sample cooling were needed in either operation mode.

Gallium metal samples with a melting point below 30°C can only be analyzed in pulsed mode, taking advantage of the much lower power requirements compared to DC operation to avoid melting. With the current instrument setup, sample cool down was manual and rather slow, so that sample turnaround was not significantly higher than with previously used cryo-cooled GD-MS instrumentation (VG9000).

In order to provide a tool for close onsite quality control in Ga industry, and for the emerging market of thin-film CIGS solar cells, a Gallium Kit is developed for the Element GD™ Plus GD-MS.

This poster summarizes first results of the workflow solution for a simple and clean sample preparation, providing a faster sample cooling and automatic warm-up after analysis for high sample turnaround times.



INTRODUCTION

Gallium as a high purity metal is an important dopant for the semiconductor industry. Purities required are in the range of 6N to 7N and higher, making these materials some of the highest metal purities available. Rather recently, the analytical demand has changed due to the start of producing thin-film solar cells on a larger scale, involving Gallium as an ingredient. QC testing needs to be done before the cells are produced in larger batches, so that a fast analytical method is required. Solid sampling is the strategy of choice due to its relative ease to avoid contamination. GD-MS as a high mass resolution technique has virtually no blank signals to consider, making it ideally suited for acquisition at lowest levels in highest purity materials. This avoids prolonged wash and blanking procedures as would be required by wet chemical ICP-MS techniques. With the development of a sophisticated method for fast flow GD-MS (source schematics in Figure 1), sample throughput for gallium analysis can be improved.

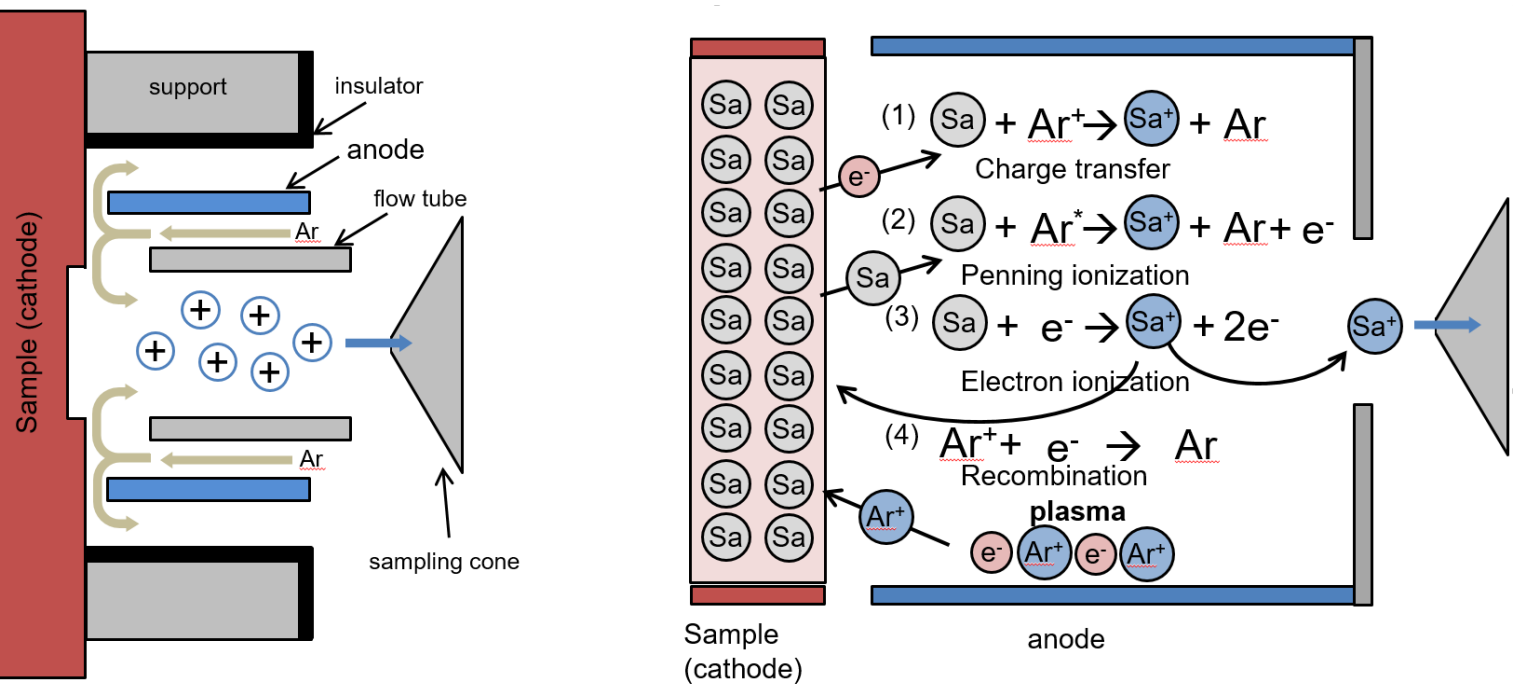


Figure 1. Schematics of a fast flow GD-MS source (courtesy of Dr. Sehoon Jung, RIST, Pohang, South Korea)



Figure 2. The Thermo Scientific Element GD Plus GD-MS.

MATERIALS AND METHODS

Instrumentation

For sample analysis, the Thermo Scientific™ Element GD Plus GD-MS (Figure 2) was used. The regular instrument features a built-in Peltier cooling for removing heat generated during the glow discharge process. Analytically, a sample cooling is usually not required, and the sample temperature does not noticeably affect analytical results. For the newly developed Gallium Kit, the cooling device in the GD sources has been re-enforced. The temperature range is extended from the previously achievable -25°C to below -35°C. This rather small extension nevertheless enables the power of the glow discharge to achieve the optimum range, yielding significantly elevated signal intensities. Besides the extended cooling range, further measures are implemented to avoid condensation of moisture on cold metal parts. Further software functions will enable a comfortable and fast sample exchange, including automated cool-down and warm-up cycles.

Method development

Parameters used are listed in Table 1. Discharge conditions have been set to achieve the strongest Ga matrix signal, while at the same time preventing sample melting due to local heat input of the GD plasma. This setup is close to initial data reported earlier ¹⁾. As a provisional setup, the default discharge voltage of 1000V was used at 20 μ s pulse duration. The resulting discharge current of ~10mA is equivalent to 10W power dissipated during the discharge. This low amount of energy is easily removed by the Peltier cooling.

Table 1. Instrument parameters used for gallium analysis

Parameter	Value
Discharge Voltage [V]	1000 (set value)
Discharge Current [mA]	~10
Discharge Gas [mL/min]	500
GD Source Pressure [mbar]	1.0
Extraction [V]	-2000
Focus [V]	-1000
Pulse Duration [μ s]	20
Pulse Frequency [kHz]	2
Source Temperature [°C]	~ -30
Matrix sensitivity [cps] ⁶⁹ Ga+ ⁷¹ Ga (MR)	1 x 10 ¹⁰

The goal for optimization is to reach a complete analysis within 40 min per sample, including cool down, warm up, and sample change times. Details of the workflow are given in Table 2.

Table 2. Workflow proposed for sample preparation and analysis

Cleaning PTFE mould; dry & store
Melt sample on warm plate
Pipette 14g of liquid Ga into mould and cover
Solidify in deep freezer
Load into GD holder, pump down & cooling routine
Presputter time: ~ 15 min
Acquisition time: ~ 15 min
Run warm-up routine for venting & sample change.

A matrix signal at the 10¹⁰cps (1.6 x 10⁻⁹ A) level is achieved, calculated as the total of both Ga isotopes in Medium Resolution (Figure 3). This value matches the default (Cu) sensitivity specification of the Element GD Plus.

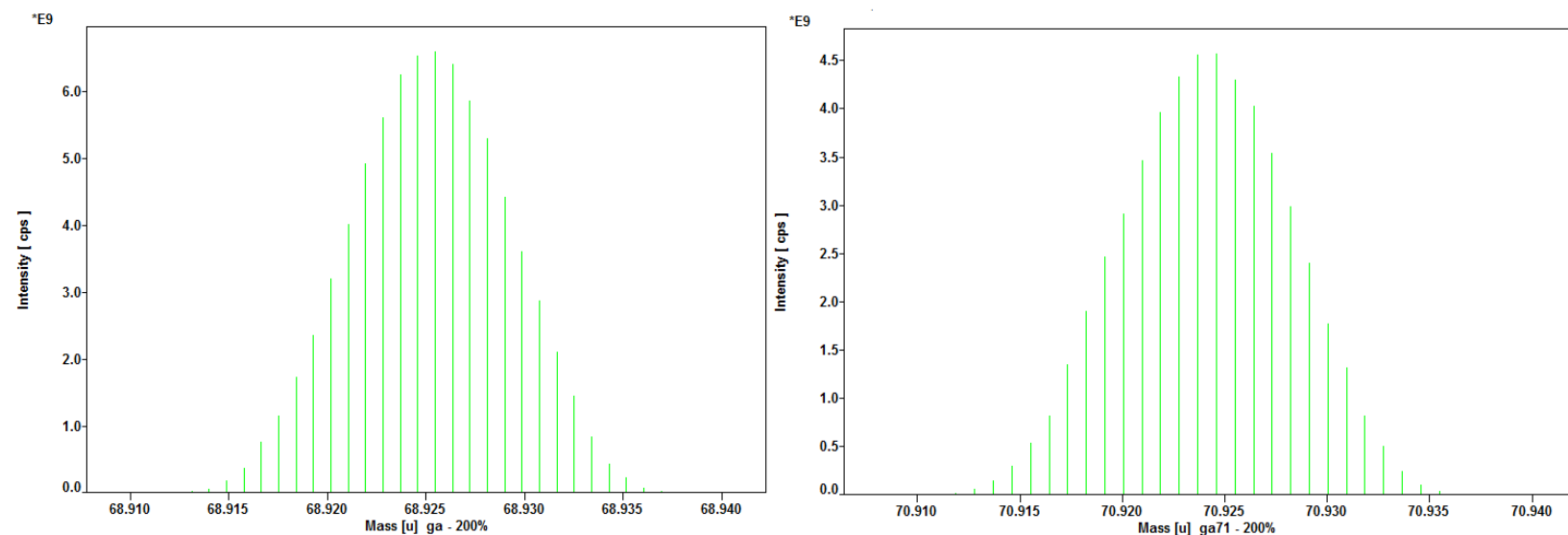


Figure 3. Matrix signals for both Ga isotopes in Medium Resolution on the Thermo Scientific Element GD Plus GD-MS.

RESULTS

As is common practice in GD-MS, a set of 74 elements is analyzed for their semiquantitative concentrations, covering most of the periodic table. For the majority of isotopes, Medium Resolution (R=4000) is applied to remove most polyatomic interferences. It is still a challenge, especially on the commonly used cryo-cooled, high-vacuum GD-MS instrumentation such as the VG9000, to safely quantify all elements free of interference. This is because GD-MS does usually not use blank correction, while generating relatively high levels of polyatomic interferences. As a consequence, manual baseline corrections are required for typical analyses.

For higher throughput and routine use, the Element GD Plus uses a straightforward approach to enable largely automated evaluation of acquired data by:

- Orders of magnitudes lower formation rate of polyatomics due to the fast-flow GD source design (Table 3)
- Trimeric interferences are virtually not existing on the Element GD Plus (Table 3), giving clean spectra that are easy to integrate
- Routine use of higher mass resolution (HR = 10000) for baseline separation of interferences that exceed the capabilities of MR
- Higher sensitivity to generate larger signals, resulting in better defined peak shapes for reliable automatic integration by software.

Table 3. Formation rates of the most prominent interferences, comparing the fast-flow concept to the cryo-cooled high-vacuum concept.

Parameter	Mass	VG9000	Element GD Plus	Improvement Factor Element GD Plus vs. VG9000
		Ratio of interference relative to ⁶⁹ Ga [ppm]		Ratio VG9000 / Element GD Plus
Abundance sensitivity	70	0.8	0.02	35
³⁸ Ar ³⁶ Ar	74	1.0	0.04	28
⁶⁹ Ga ³⁸ Ar	107	25	3.5	7
⁶⁹ Ga ⁴⁰ Ar	109	1.0%	0.13%	8
⁶⁹ Ga ⁴⁰ Ar ¹² C	121	0.068	0.0001	~700
⁷¹ Ga ⁴⁰ Ar ¹² C	123	0.058	0.0001	~600

The main interferences originating from the Ga matrix show up close to the silver masses. High mass resolution is applied here to separate the analyte peak from the interference, so that no manual peak integration is required (Figure 4).

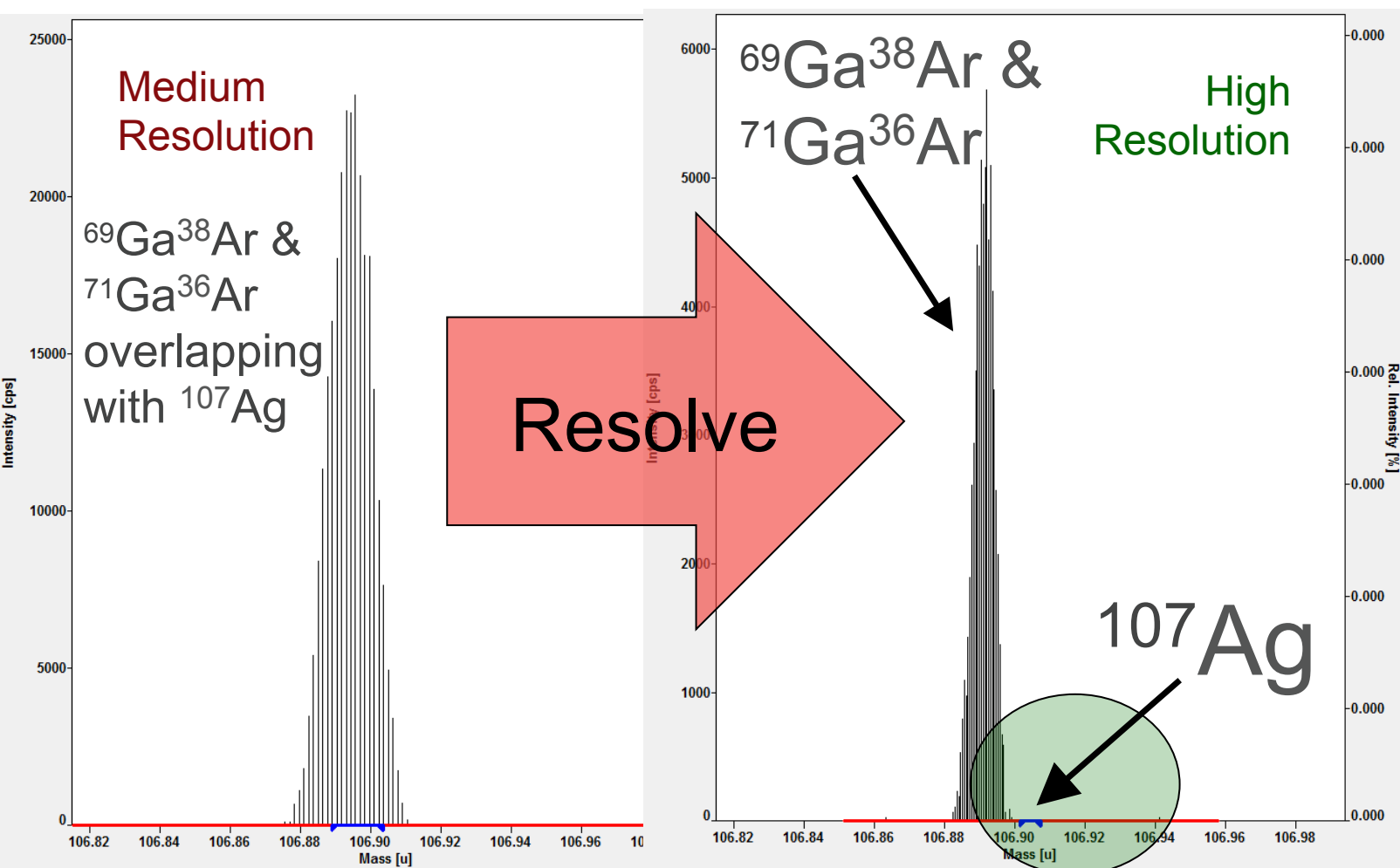


Figure 4. Spectra showing the main interference in Medium Resolution (R=4000) (left) and fully resolved using High Resolution (R=10000, right)

The purity of gallium metal is finally assessed by summing up the elemental impurities determined. Figure 5 exemplarily shows some trace metals contained in a 6N Ga sample at the ~5ppb level. The chart illustrates that a presputter time of just 15 minutes is required, proving the success of the sample preparation workflow. The final result would be the average of the concentration readings during the acquisition (Figure 5), omitting the presputter time.

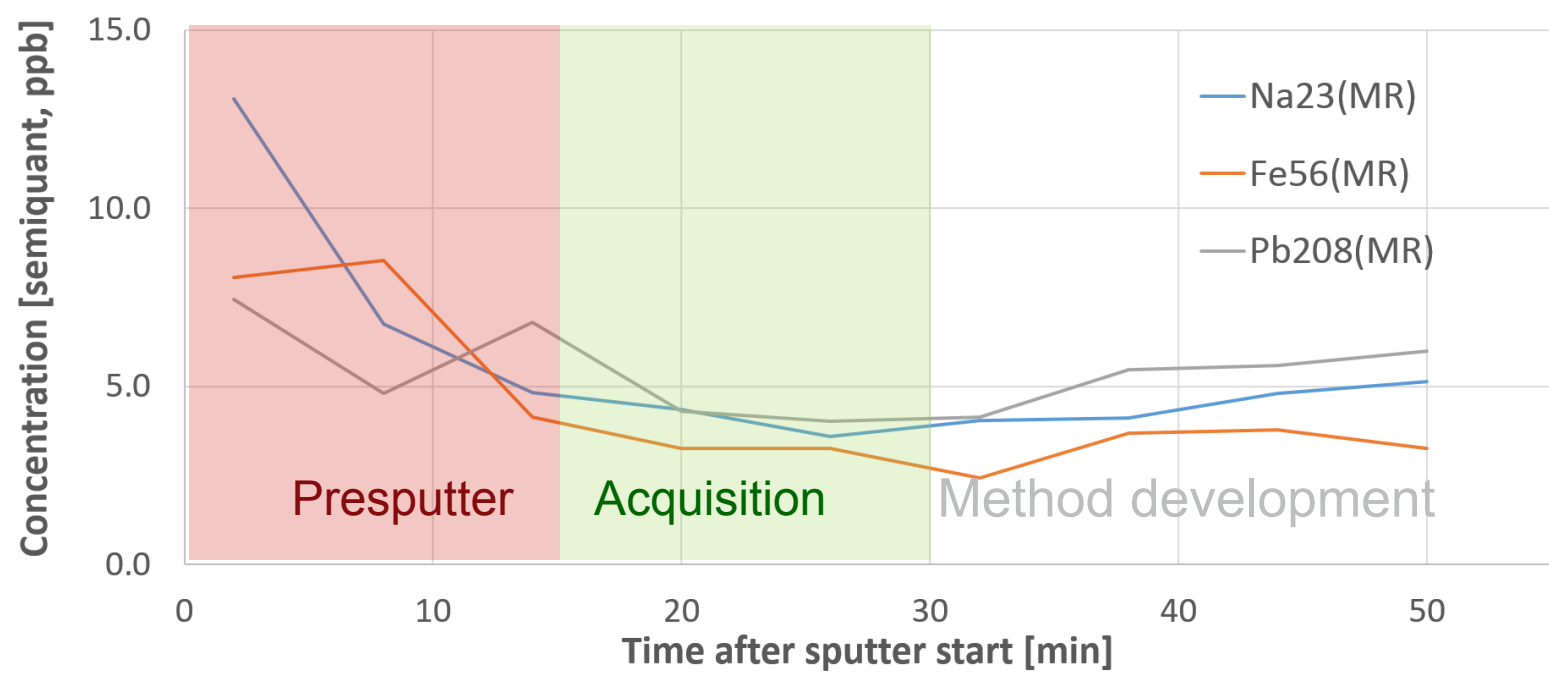


Figure 5. Presputter behavior at ultra-trace level (concentrations ~ 5 ppb). The colored intervals show the presputter and acquisition period used for routine operation.

CONCLUSIONS

The Thermo Scientific Element GD Plus with the newly developed Ga kit is a valuable tool for trace metal analysis of high purity gallium. There is no need to apply liquid nitrogen for cryogenic cooling, improving the handling and increasing the speed of analysis. The workflow solution offers easy, clean and fast analyses, which is of high importance in industries as a key factor in cost efficient quality control.

REFERENCES

1. Poster presented at Winter Plasma Conference 2011: Development of a Pulsed DC-GD-MS instrument. Joachim Hinrichs, G. Churchill, K. Putyera, L. Rottmann, M. Hamester.

ACKNOWLEDGEMENTS

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