

# Analysis of Solar Cell Silicon Using Glow Discharge Mass Spectrometry

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## Introduction

The ever-increasing demand for alternative energies has triggered a significant increase in the demand for high purity solar cell silicon and a subsequent need for analytical techniques, which can deliver accurate data in the shortest analysis times possible to allow close production control. The Thermo Scientific ELEMENT GD is the first instrument of its kind to allow short turnaround times of less than 20 minutes for the analysis of solar cell silicon.

Impurities in solar cell silicon are crucial because they limit the photovoltaic efficiency of the solar cell. The ELEMENT GD is capable of directly determining impurities in photovoltaic solar cells at single digit ppb detection limits, and even lower than 1 ppb for many elements.

For this particular application, the ELEMENT GD was used to quantify trace element concentrations in solar cell silicon. Due to the variable resolution setting, many elements were analyzed in the most sensitive low resolution mode as no polyatomic interferences were observed. Most other elements were analyzed in medium resolution mode and high resolution mode for selected cases. The results demonstrated that the major interferences originate from polyatomic combinations of the matrix element silicon with the discharge gas Argon. It was also observed that at the ppb level the analyte concentrations were decreasing for less than 10 minutes. Therefore, a pre-sputter time of 12 minutes was chosen. The analysis time was set to 6 minutes.

TABLE 1. Sample preparation.

Grind Si sample into shape
Grind sample surface (grid 120 followed by grid 220 diamond grinding discs; HD Piano, Struers GmbH, Germany)
Wash surface with deionised water
Clean surface from grinding contaminations with 10% ultrapure HNO <sub>3</sub>
Wash surface with deionised water
Dissolve top layer of surface with 20% ultrapure HF
Wash surface with deionised water
Rinse with isopropanole
Dry

TABLE 2. Instrumental settings.

Discharge current	65 mA
Discharge voltage	~ 1000 V
Discharge gas	400 ml Ar min <sup>-1</sup>
Matrix sensitivity	1 x 10 <sup>10</sup> cps (Medium Resolution)
Anode material	Steel
Anode cap and flow tube	Graphite
Cone	Graphite

## Method

During method development, the best choice of resolution settings, isotopes and measurement duration was investigated to achieve ultralow detection limits at high sample throughput. Major interferences originated from polyatomic combinations of the matrix with the discharge gas Argon (Table 3), and the dimer of the matrix element.

TABLE 3. Major interferences.

Affected isotope	Interference
<sup>56</sup> Fe	<sup>28</sup> Si <sup>28</sup> Si
<sup>64</sup> Zn	<sup>28</sup> Si <sup>36</sup> Ar
<sup>66</sup> Zn	<sup>28</sup> Si <sup>38</sup> Ar
<sup>66</sup> Zn	<sup>30</sup> Si <sup>36</sup> Ar
<sup>68</sup> Zn	<sup>30</sup> Si <sup>38</sup> Ar
<sup>68</sup> Zn	<sup>28</sup> Si <sup>40</sup> Ar

While the formation rates of <sup>28</sup>Si<sup>36</sup>Ar (1 ppm) and <sup>28</sup>Si<sub>2</sub> (0.1 ppm) relative to the Si matrix signal were found to be low, it would nevertheless result in erratic results for Zn and Fe when applying just nominal mass resolution. The interference peaks were resolved from the analytes using Medium Resolution (Figure 1 and 2), and did therefore not disturb the quantification of Zn and Fe.

FIGURE 1. Medium Resolution scan (R=4000) of <sup>64</sup>Zn<sup>+</sup> resolved from <sup>28</sup>Si<sup>36</sup>Ar<sup>+</sup>.

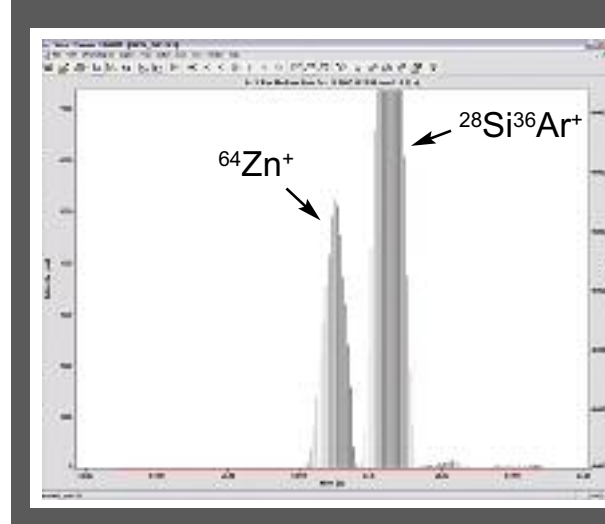
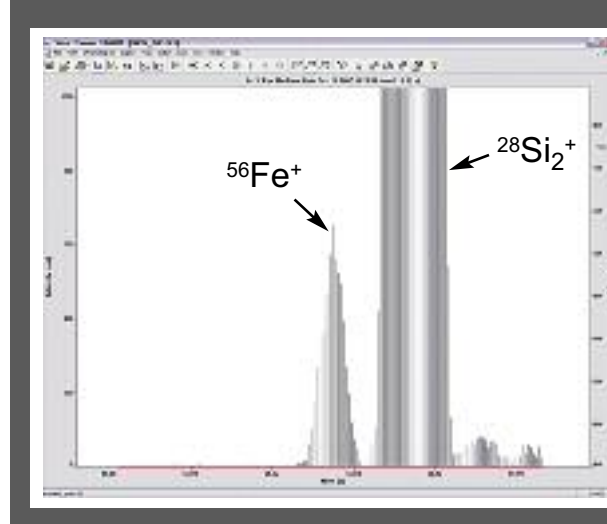


FIGURE 2. Medium Resolution scan (R=4000) of <sup>56</sup>Fe<sup>+</sup> resolved from <sup>28</sup>Si<sub>2</sub><sup>+</sup>.



As a last step of method development, the pre-sputter time necessary was evaluated by monitoring the measured concentrations over time. While the matrix signal was stable after several minutes, some analytes present at the ppb level (especially Na and Zn) were decreasing over ~ 10 minutes due to remaining impurities of sample surface grinding. Therefore, the pre-sputter time was set to 12 minutes for the following analyses. The analysis time of 6 min was sufficient to achieve good counting statistics at the ultratrace level considered. Method settings and results are presented in Table 4.

TABLE 4: Results and detection limits obtained for repeated Si analysis on 5 individual spots. LR = Low Resolution, R = 400; MR = Medium Resolution, R >= 4000, HR = High Resolution, R >= 10000.

Element	Mass	Resolution	Average n = 5 spots conc [ppb]	LoD (3 s) n = 5 spots conc [ppb]
Li	7	LR	< LoD	0.10
Be	9	MR	< LoD	2.5
B	11	MR	28.0	6.7
Na	23	LR	0.6	0.4
Mg	24	MR	< LoD	0.14
Al	27	MR	0.8	0.6
P	31	MR	16.0	6.5
K	39	HR	1.7	1.0
Ca	44	MR	< LoD	3.6
Sc	45	MR	< LoD	0.06
Ti	48	MR	< LoD	0.07
V	51	MR	< LoD	0.02
Cr	52	MR	< LoD	0.10
Mn	55	MR	< LoD	0.08
Fe	56	MR	0.4	0.3
Ni	58	MR	< LoD	0.5
Co	59	MR	< LoD	0.08
Cu	63	MR	1.8	1.1
Zn	64	MR	4.1	3.2
Ga	71	HR	< LoD	2.2
Ge	72	HR	1.6	0.4
As	75	MR	0.5	0.5
Se	77	MR	6.9	4.6
Rb	85	MR	< LoD	0.5
Sr	88	MR	< LoD	0.13
Y	89	MR	< LoD	0.12
Zr	90	MR	< LoD	0.17
Nb	93	MR	< LoD	0.10
Mo	95	MR	< LoD	1.2
Ru	102	MR	< LoD	0.24
Rh	103	MR	< LoD	0.21
Pd	105	MR	< LoD	1.4
Ag	107	MR	0.3	0.3
Cd	111	MR	2.5	2.4

TABLE 4. (continued)

Element	Mass	Resolution	Average n = 5 spots conc [ppb]	LoD (3 s) n = 5 spots conc [ppb]
In	115	LR	2.0	0.3
Sn	117	LR	1.2	1.1
Sb	121	MR	1.3	0.7
Te	126	MR	1.9	1.8
Cs	133	LR	0.09	0.07
Ba	138	LR	< LoD	0.03
La	139	LR	< LoD	0.03
Ce	140	LR	0.10	0.09
Pr	141	LR	0.05	0.04
Nd	143	LR	< LoD	0.3
Sm	152	LR	0.4	0.3
Eu	153	LR	0.03	0.02
Gd	158	LR	< LoD	0.14
Tb	159	LR	< LoD	0.04
Dy	164	LR	< LoD	0.25
Ho	165	LR	< LoD	0.03
Er	166	LR	0.04	0.03
Tm	169	MR	< LoD	0.15
Yb	173	LR	< LoD	0.19
Lu	175	LR	< LoD	0.02
Hf	178	LR	0.04	0.03
Ta	181	LR	2.7	2.5
W	184	LR	< LoD	0.12
Re	187	LR	< LoD	0.19
Os	189	LR	< LoD	0.27
Ir	193	LR	< LoD	0.10
Pt	195	LR	< LoD	0.18
Au	197	LR	< LoD	0.8
Hg	202	LR	< LoD	0.9
Tl	205	LR	< LoD	0.14
Pb	208	LR	0.09	0.08
Bi	209	LR	< LoD	0.14
Th	232	LR	< LoD	0.048
U	238	LR	< LoD	0.023

## Results

All results given have been measured as ion beam ratios and converted to bulk concentrations by applying the respective calibration factor from the Thermo Scientific ELEMENT GD Standard RSF table. This approach is common practice in GD-MS analysis, giving semiquantitative results that typically fall within 30% of the true values. Due to the lack of certified low-level silicon reference materials, all data shown in Table 4 were evaluated semiquantitatively. From the analysis of the purest material available, an estimate of detection limits can be obtained from repeat analysis at 5 different spots (Table 4). Typically the LoD's are below the ppb level, being mostly limited by the signal to noise ratio of approximately 0.2 cps vs. 1 x 10<sup>10</sup> cps (background noise versus matrix sensitivity in Medium Resolution) giving a theoretical value of 20 ppt. For example, the Medium Resolution measurement of vanadium gives a LoD of 20 ppt. Elements that yield worse detection limits generally suffer from bad isotopic abundances of the isotopes that had to be used, e.g. <sup>44</sup>Ca, <sup>77</sup>Se, and <sup>111</sup>Cd.

## Conclusion

The direct bulk GD-MS analysis of the most important trace elements in solar cell silicon (Mg, Al, Ca, Ti, V, Cr, Fe, Ni, Cu, As, Zr) show typical detection limits well below or around 1ppb. These LoD's were obtained with minimum sample preparation effort restricted to grinding and acid cleaning of the sample surface. All concentrations measured are semiquantitative because Standard RSF's have been used. Nevertheless, the relative variations between samples will be accurate, therefore providing a valuable tool for production and contamination control in solar cell industry.

