

## Comparison of Solar-Grade Silicon Analytical Methods for Metallic Contamination

Concerns with impurities in solar-grade silicon have been discussed both academically and within commercial arenas for over 20 years. Although more forgiving than silicon used in integrated circuit semiconductor processes; solar-grade silicon (SoGSi) and ultimate photovoltaic efficiency can still be affected via minority carrier lifetime if impurities are above a certain contamination threshold. Numerous studies in the literature have shown photovoltaic efficiency is affected by impurities; the art within the industry has been to find a silicon source that is “pure enough” for solar cell manufacturing without approaching the higher cost of semiconductor-grade silicon material. With considerable emphasis placed on solar energy in the last 2-3 years, and with crystalline or amorphous silicon representing more than 80% of current solar technologies, the need for expedient and low level metallic impurity analysis has increased. In this brief article we will compare and contrast Glow Discharge Mass Spectrometry (GD-MS) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) as a means to easily quantify metallic contamination in bulk silicon samples.

Techniques used to measure impurities in silicon have existed via earlier semiconductor applications for many years, and include photoluminescence, Fourier transform infrared spectroscopy and neutron activation analysis. These all provide a technique for certain contaminants, but suffer in the ability to provide analysis for a broad range of metallic impurities at consistent detection limits or simply can be expensive and time consuming analyses. GD-MS and ICP-MS are different, as essentially all metallic elements in the periodic table can be measured in a straight-forward manner with both techniques. Although both instruments ultimately utilize mass spectrometry as their detector of choice, the means of sample prep, quantitation and analysis are completely different and affect some analytical figures of merit. A quick summary of GD-MS and ICP-MS is shown in Figure 1 below.

Analytical Figure of Merit	GD-MS	ICP-MS
Element Coverage	Metallic elements plus B, P	Metallic elements plus B, P
Calibration Technique	Uses reference material where available to establish sensitivity	Uses NIST traceable standards to quantify all elements
Detection Limits	1-50 ppb	ppt levels, 20 ppt and up
Spiked Samples Available for QC	Not easily performed	Straight-forward to perform

Figure 1: A brief summary of GD-MS and ICP-MS figures of merit

### Sample Preparation

Both techniques allow for the analysis of silicon in chunks, flakes, granules, powders, etc. Preparation for GD-MS involves the incorporation of silicon along with a matrix medium, e.g. graphite or indium, into a final sample pin. This pin then serves as a cathode in a glow discharge plasma generation process forming ions for detection. The ICP-MS sample process involves dissolving a silicon sample in high purity hydrofluoric acid matrix which is then incorporated into a conventional ICP-MS system.

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## Element Coverage

Both techniques permit almost instantaneous elemental analysis across the periodic table. In addition, important elements like boron and phosphorus are also covered with both techniques. GD-MS and ICP-MS can both be plagued by potential mass interferences and require talented chemists to avoid false positives. This is not a trivial aspect of the analysis, and care should be taken in choosing any lab utilizing GD-MS or ICP-MS.

## Calibration Technique

In this area the two techniques differ quite substantially. With ICP-MS, silicon is dissolved in an aqueous acidic matrix. This same acidic matrix is then used for preparing blanks and standards with widely available NIST-traceable standards. Thus with every sample there is a blank and standards that are used to generate a calibration curve and permit quantitation. Thus once the silicon material is adequately sampled and in solution the analysis becomes much like any other ICP-MS measurement. GD-MS, because there are relatively few NIST-traceable standards in the solid phase, does not permit such an easy calibration for every sample. Relative sensitivity factors are established in separate analyses and the instrument is calibrated with reference materials where such reference samples exist.

## Detection Limits

Although both techniques utilize mass spectrometry for their detection technique, the difference in sampling, ionization and instrument design affect the ultimate detection limit available. ICP-MS has been used to measure part-per-quadrillion levels for some samples, and detection limits to the low part-per-trillion (ppt) are available for analysis of silicon samples. GD-MS samples (sputters) and ionizes in a different manner, and can reach low part-per-billion type analyses. For some obscure elements GD-MS might reach lower detection limits, however the ultimate lower detection limits with ICP-MS are preferable.

Elements	GD-MS	ICP-MS
	ppb (ng/g)	ppb (ng/g)
Na	10	0.1
Mg	5	0.1
Al	10	0.1
K	50	0.1
Ca	50	0.1
Ti	5	0.1
Cr	10	0.1
Mn	5	0.1
Fe	10	0.1
Co	5	0.1
Ni	10	0.1
Cu	10	0.1
Zn	50	0.1
As	10	0.1
Sr	10	0.1
Zr	10	0.1
Mo	50	0.1
Sn	10	0.1
Sb	10	0.1
Ba	10	0.1
Pb	10	0.1

Figure 2: Typical detection limits for routine metallic impurities in bulk silicon analysis by GD-MS and ICP-MS

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### QC of Sample Results

A unique advantage of the sample preparation and calibration technique with ICP-MS is that samples can easily be spiked with NIST-traceable concentrations for each element of interest. In this manner a known concentration of each element can be added to a sub-sample of the final liquid sample and analyzed versus the NIST-generated calibration curve. Thus if one adds 25 ppb of Fe to a dissolved silicon sample, does one measure 25 additional ppb of Fe in that spiked sample? As the example illustrates in Figure 3, this type of experiment allows a very straight-forward manner in which the accuracy and quality of the sample results can be judged, and asking a laboratory for spike results should be every customer's prerogative when judging the accuracy of their sample results. Because GD-MS generates a final sample into a solid pin, this type of experiment cannot be easily performed for all elements in an analysis scheme.

Element	Si Sample	Spike Amt	Measured	Recovery %
Na	5.6	25	25	82
Al	8.8	50	63	107
K	3.3	16	16	83
Ca	4.7	50	64	117
Ti	1.5	16	15	86
Cr	2.4	16	16	87
Mn	0.1	16	16	99
Fe	7.2	16	15	65
Co	0.2	16	16	99
Ni	3.3	16	16	83
Cu	5.7	50	57	102
Zn	2.0	16	15	83
Mo	4.7	50	60	110

Figure 3: ICP-MS results in unit of ppb (w/w) illustrate spike recovery to check for quality control. SEMI dictates good recovery as between 80 and 120%.

### Summary

Both GD-MS and ICP-MS can be utilized to analyze bulk silicon samples in a variety of forms. The bottom-line outcome is to establish if silicon meets a particular specification for manufacturing efficient photovoltaic cells. The advantages ICP-MS provides include sensitivity, NIST-traceability with every analysis, and the ease in which quality control can be checked and assured with each sample. One note for the future is that beyond current specifications, the additional sensitivity allowed with ICP-MS may provide added utility as more pure forms of silicon may be required in advanced solar cell designs.

For additional information, please contact [us](#).