

Ultratrace Analysis of Phosphorus, Boron and Other Impurities in Photovoltaic Silicon and Trichlorosilane by ICP-MS with High Energy Collision Cell

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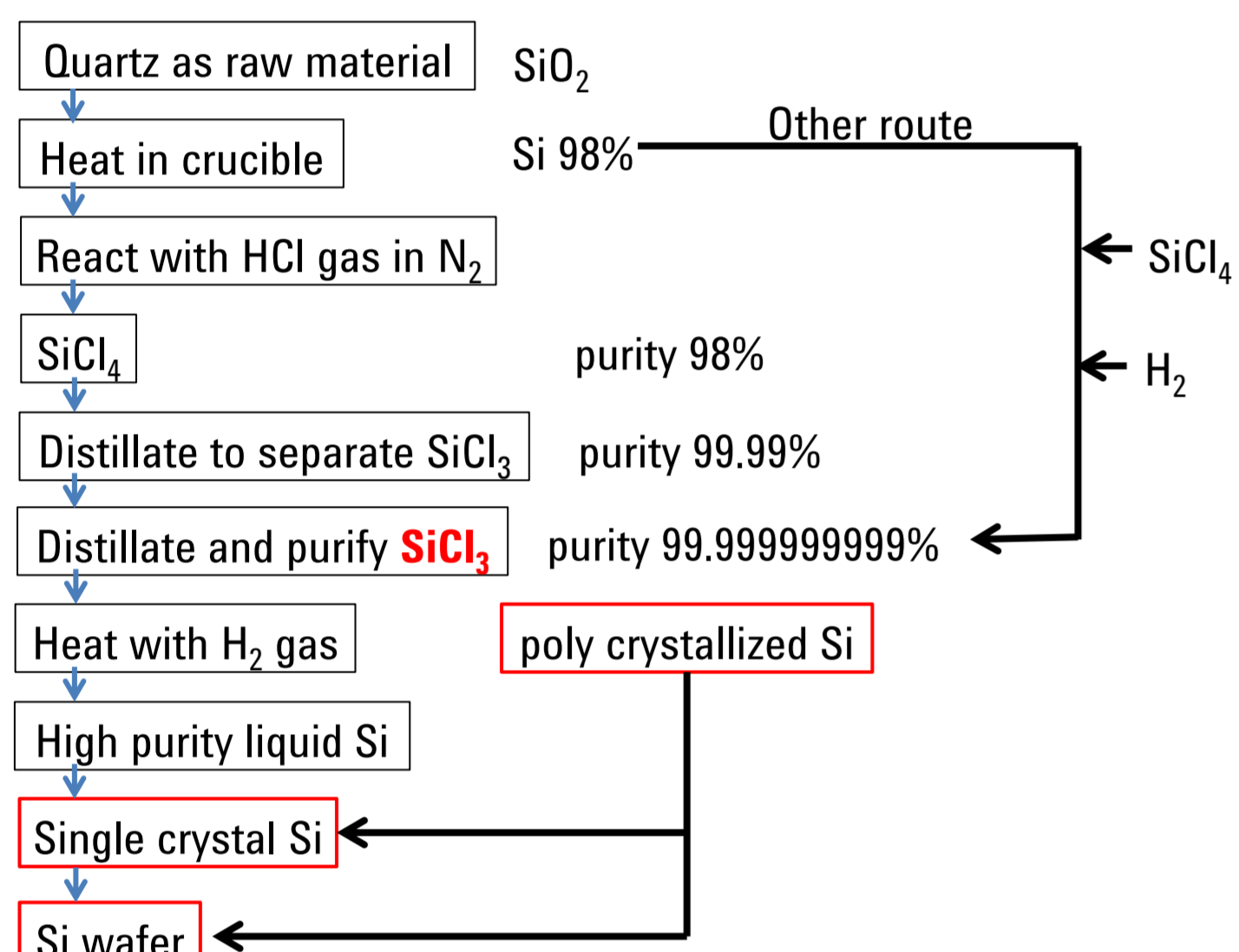
Introduction

Research for alternative energy source is now highly accelerating. One of the most dynamic areas is the development of devices to utilize solar power. The growing demand for solar power devices requires highly efficient energy converters, primarily silicon. Impurity control of photovoltaic silicon, particularly for boron and phosphorus is critical to the efficiency of the device. Although ICP-OES has been used for analysis of these impurities so far, lower detection capability is demanded. This paper describes the procedure of sample preparation and ICP-MS analysis.



Solar power experimental facility in Yamanashi, Japan

Solar grade silicon is manufactured by the following process.



Impurities of PV Si such as Si wafer, crystal Si, polysilicon and intermediate SiHCl₃ (TCS) must be monitored. Analysis of these materials have several challenging problems such as

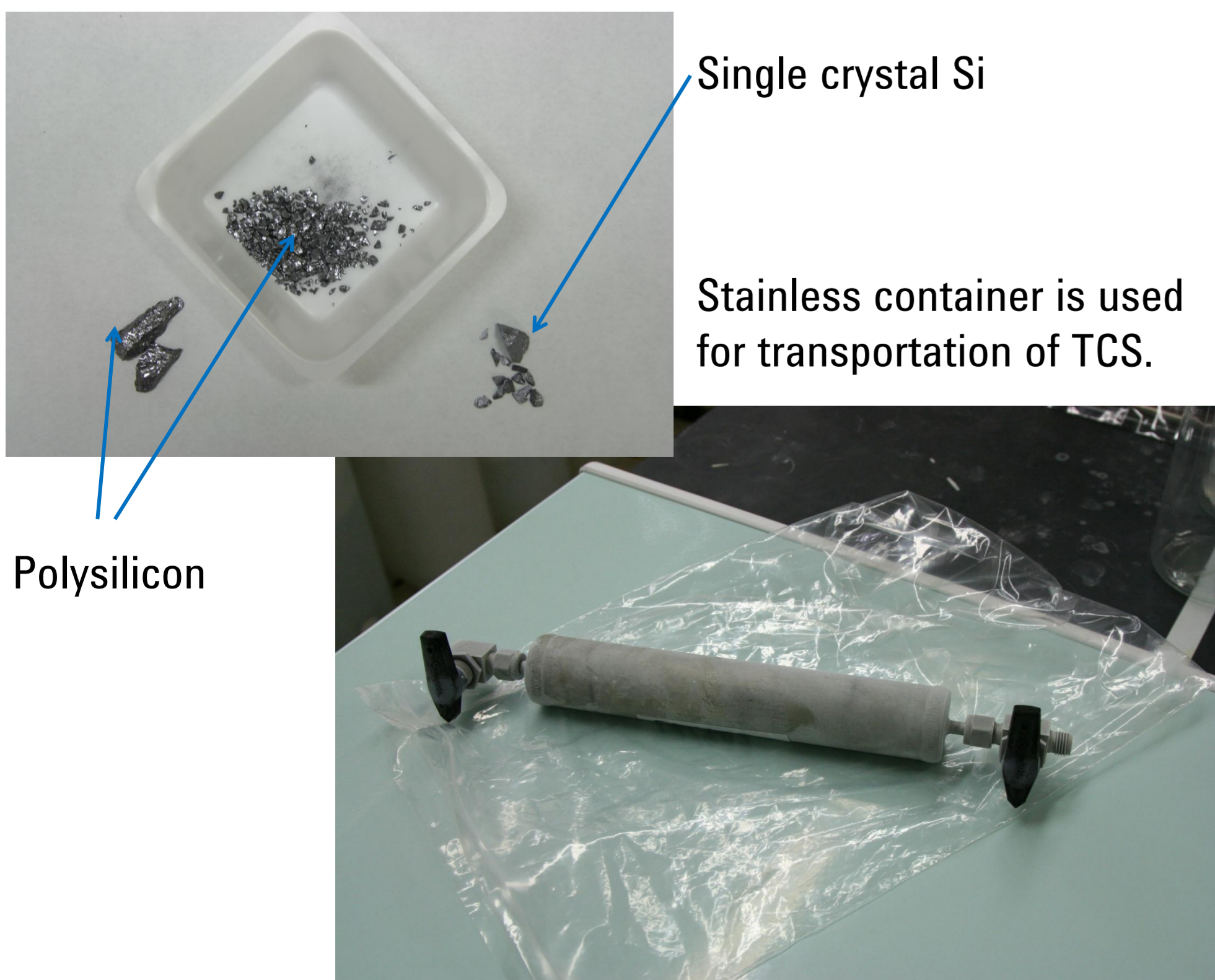
1. Concentration of impurities is ng/g (ppb).
2. The most important analytes are boron and phosphorus.
3. ³⁰SiH interferes with ³¹P determination.
4. ²⁸Si¹⁹F interferes with ³¹P¹⁶O.
5. Therefore, Si must be removed from sample solution.
6. PV Si dissolves in HF/HNO₃. Heating to dryness will vaporize Si as SiF₄. However, boron will be removed at the same time.
7. B in PV Si must be separately analyzed from other elements.
8. TCS is very volatile liquid (b.p. 31.8C°) and aggressively reacts with water in air. SiHCl₃ + 2H₂O → SiO₂ + 3HCl + H₂
9. TCS must be treated in inert and dry gas.

Experimental

Strategies for PV Si and TCS analyses are as follows.

PV Si analysis: Sample is divided to 2 groups, 1 for B and 1 for others. Mixture of HF/HNO₃ is used for digestion. In order to enhance removal of Si, a small aliquot of H₂SO₄ is added to one group for non B analysis. Presence of H₂SO₄ raises the solution temperature when heating. For B analysis, stop heating before dryness occurs. Residue after heating is recovered with diluted HNO₃ and analyzed by ICP-MS using external calibration method.

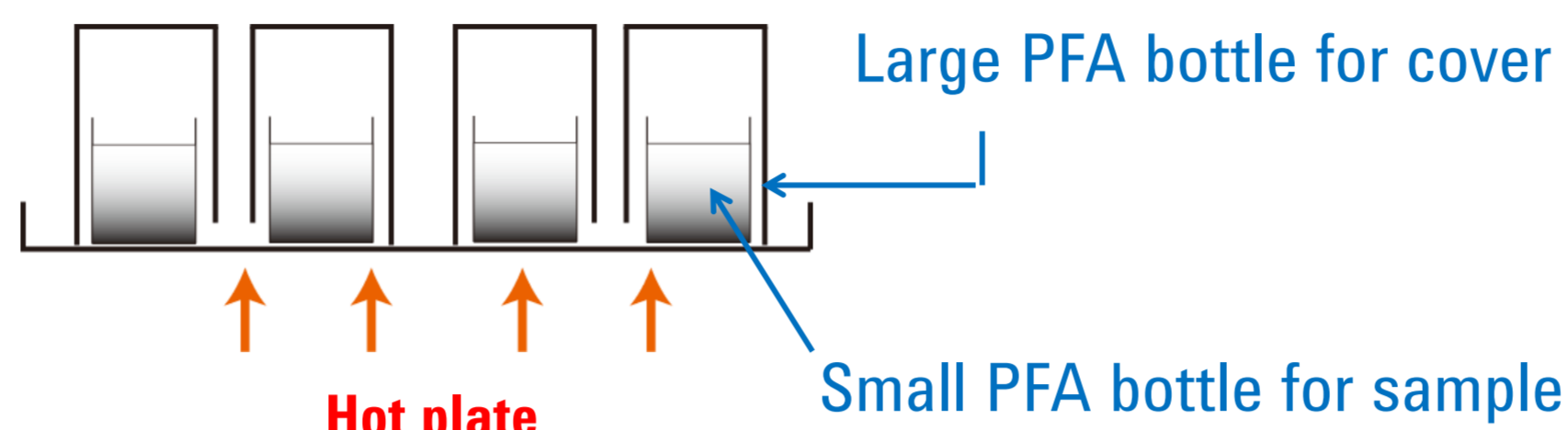
TCS analysis: Sample is converted to SiO₂ in inert environment. SiO₂ is then dissolved in HF. In order to stabilize B during heating, a small aliquot of glycerol is added to the solution. Residue is recovered with diluted HCl and analyzed by ICP-MS.



Procedure is shown below.

PV Si analysis:

1. Break silicon block to pieces with a hammer.
2. Clean sample pieces with HNO₃/HCl, UPW and HF.
3. After drying with argon gas, transfer 0.3 g sample to PFA bottle.
4. Add 0.5mL of 10% H₂SO₄ to the bottle.
For boron determination, no H₂SO₄ is added.
5. Dissolve the sample in HF/HNO₃.
6. Heat the solution to nearly dryness, *not complete dryness.*



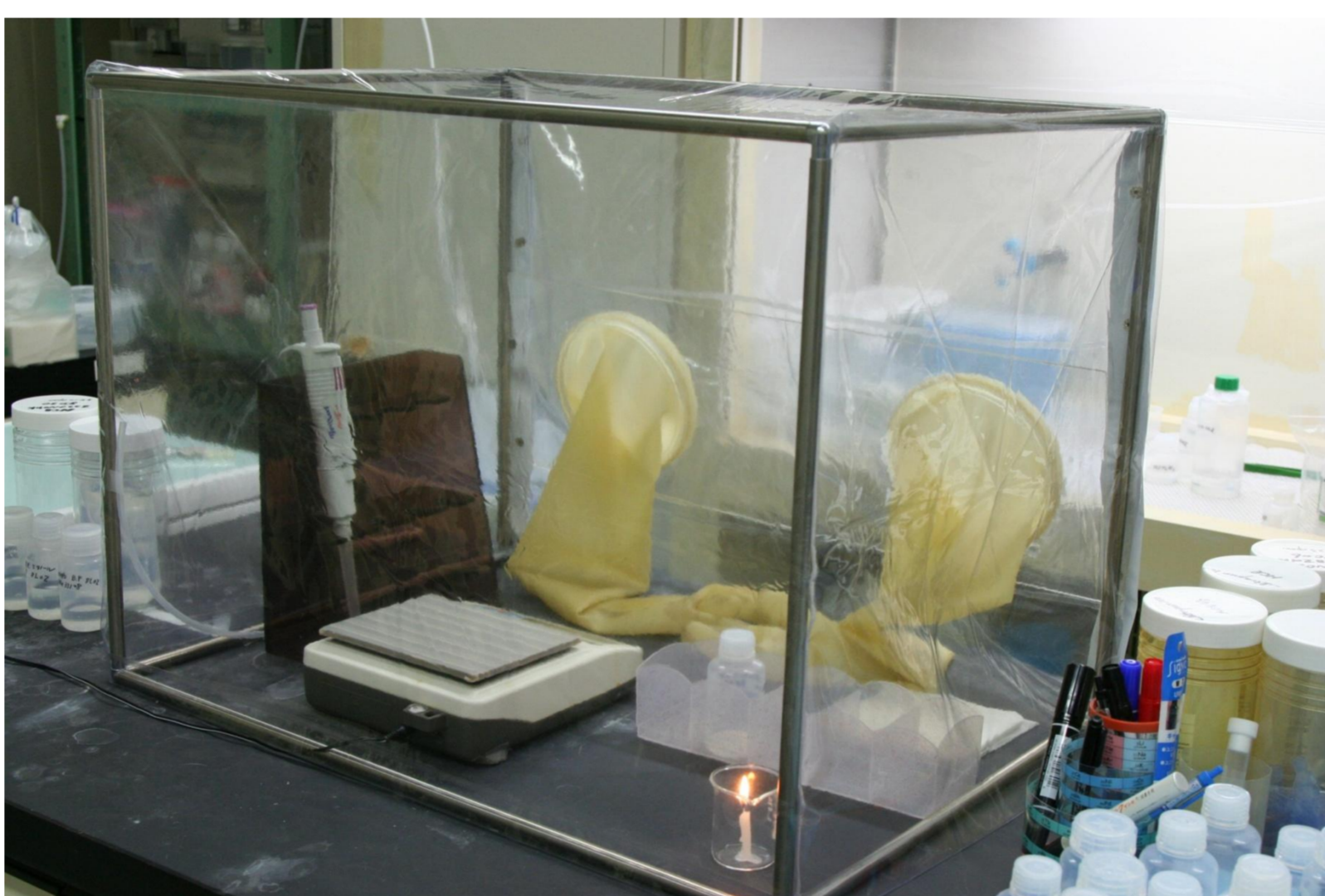
7. Dissolve the residue with 0.5% HNO₃.
8. ICP-MS analysis by external calibration method.



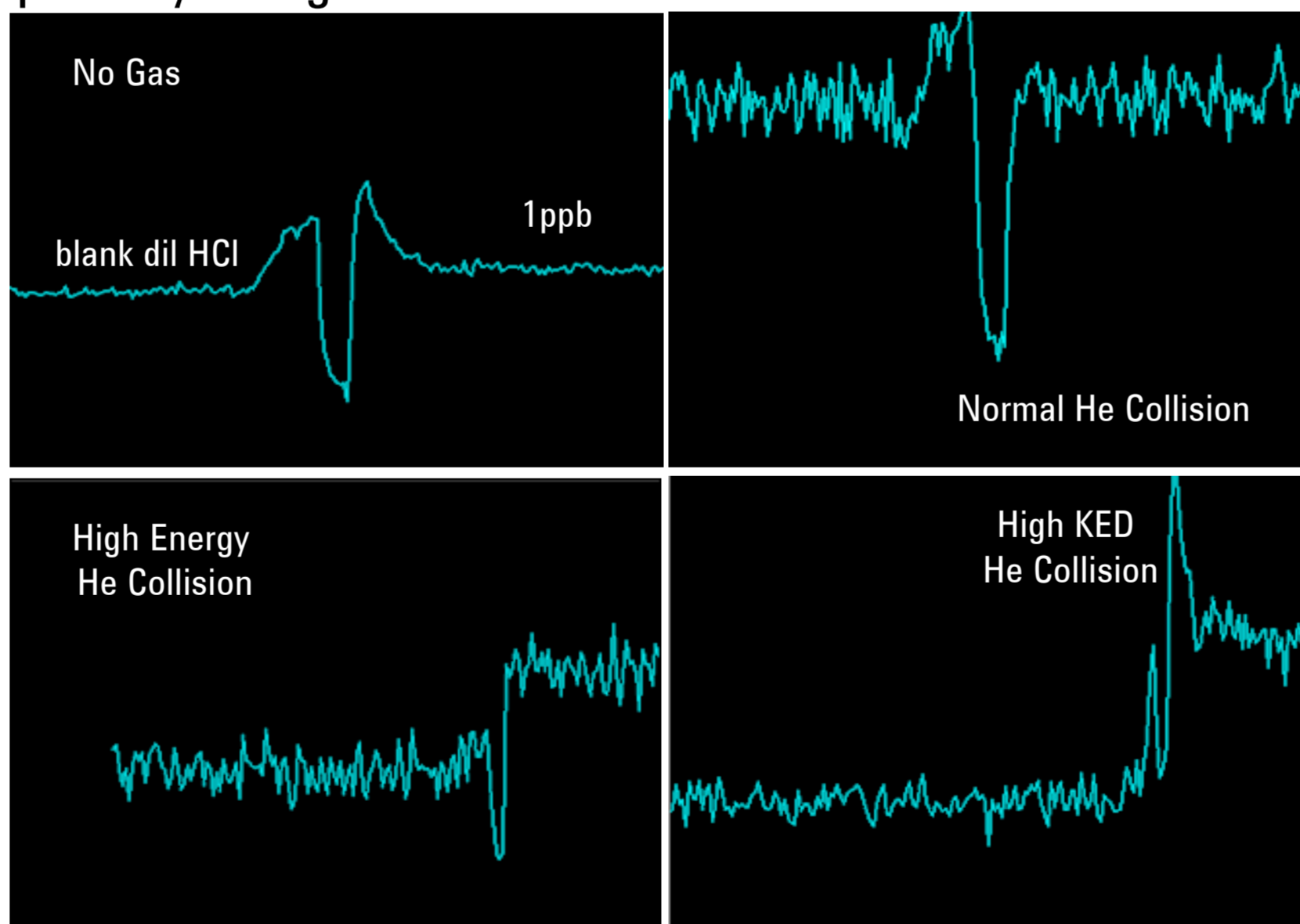
It is important to stop heating before complete dryness particularly for boron determination.

TCS analysis:

1. Prepare 3g of pure ice in 30mL PFA vial.
2. Add 1.5mL of sample (approx 2g) to pure ice in glove box.
3. Cap the vials and transfer them to clean draft.
4. After the ice melts, add 10mL of 20% HF.
5. After vigorous reaction finishes, add 1mL of 10% glycerol.
6. Heat the solution till droplets under the cover disappear.
7. Dissolve the residue with 15mL of 0.4% HCl.
8. Analyze the solution by ICP-MS.

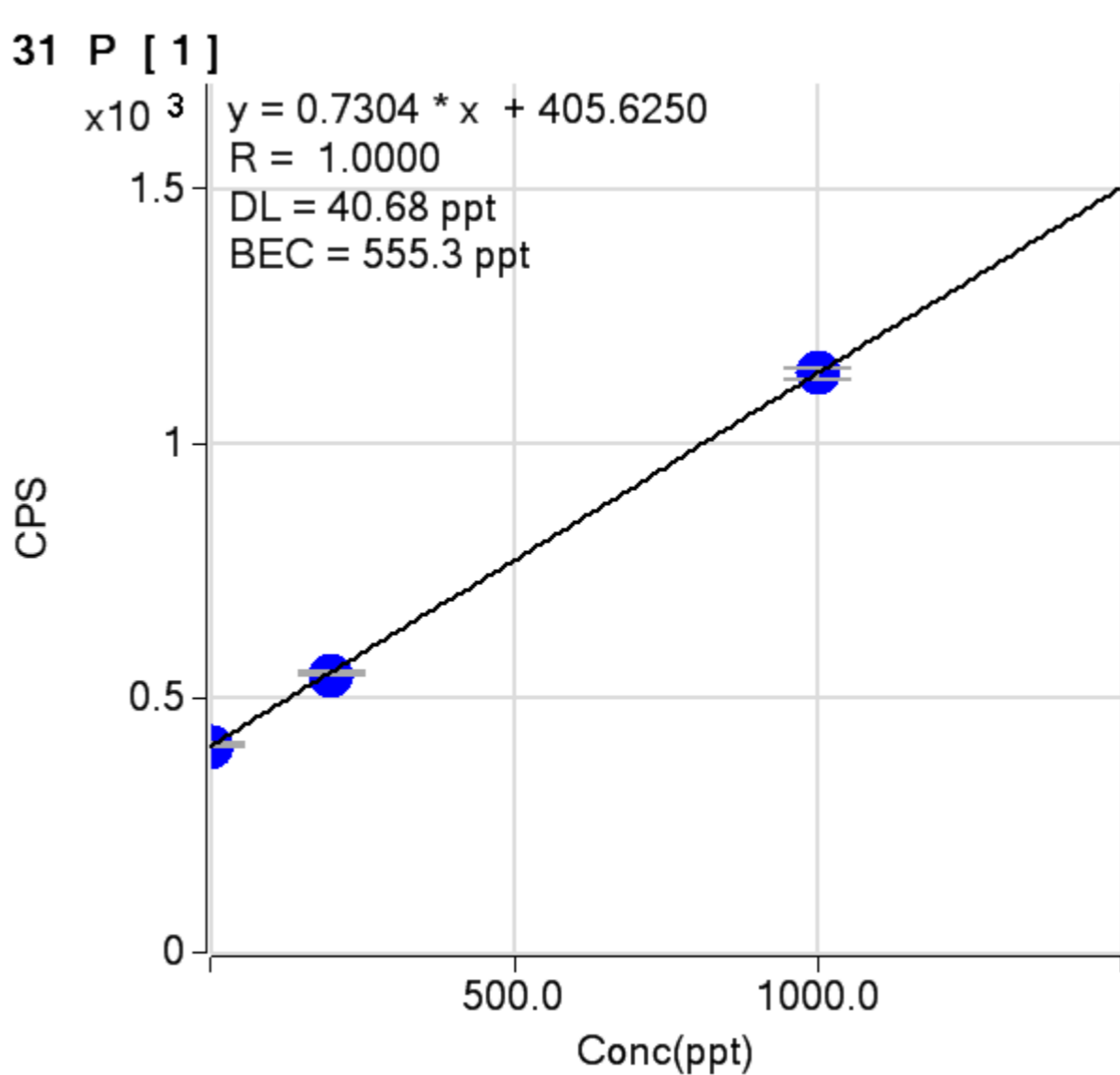


Final solution of PV contains HNO₃ which affects ³¹P intensity, therefore ³¹P¹⁶O was measured instead of ³¹P. On the other hand, solution of TCS does not contain HNO₃. Measurement of ³¹P was applied by using HCl as a diluent.



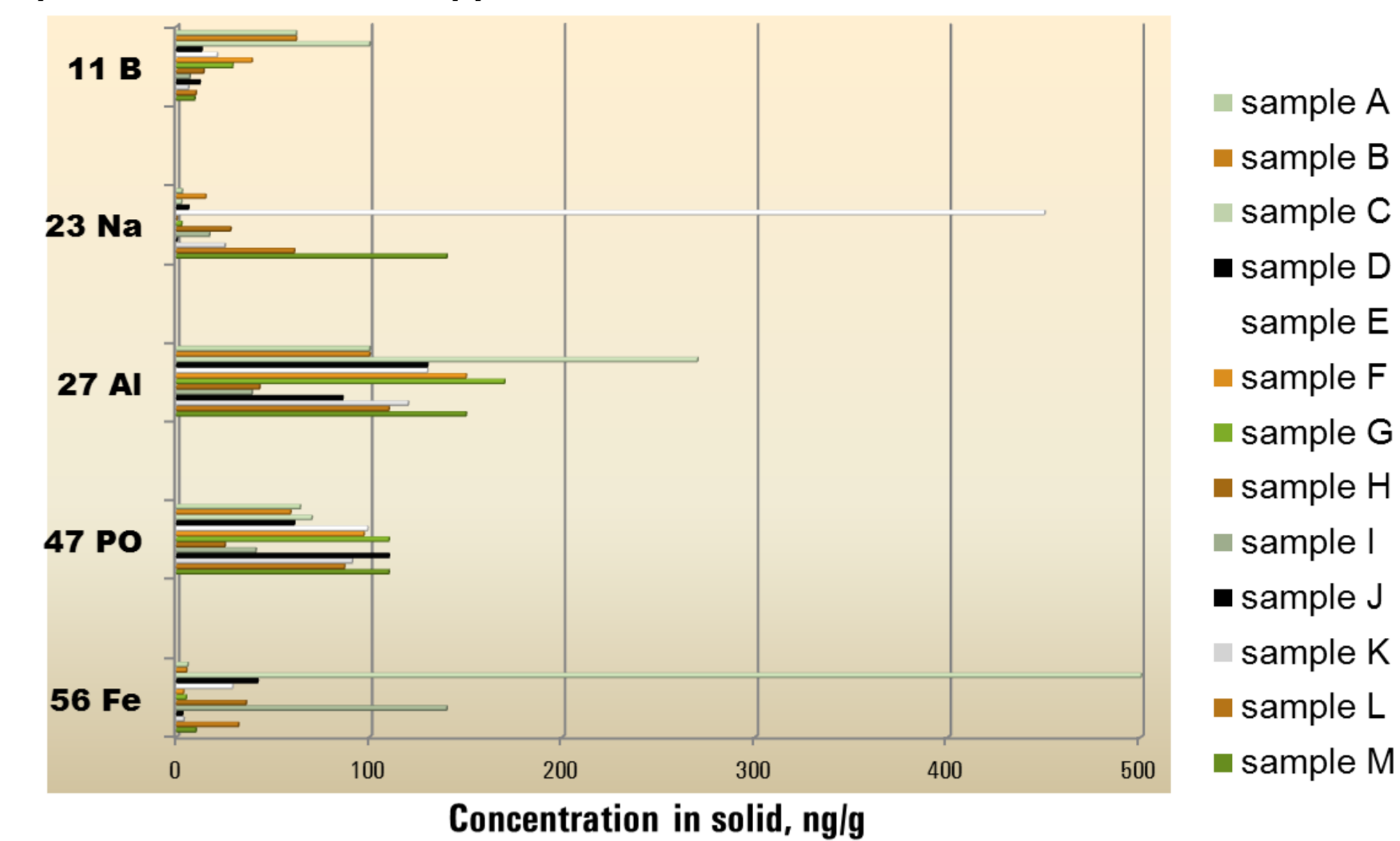
Here, 2mL/min He with 100V KED showed better results than 10mL/min He with 5V KED (cell bias voltage was -100V in both cases). No signal was found on No gas mode or normal He mode (5mL/min He, 5V KED and -18eV cell bias).

³¹P¹⁶O method provides better BEC than ³¹P method but DL below is acceptable for TCS analysis.



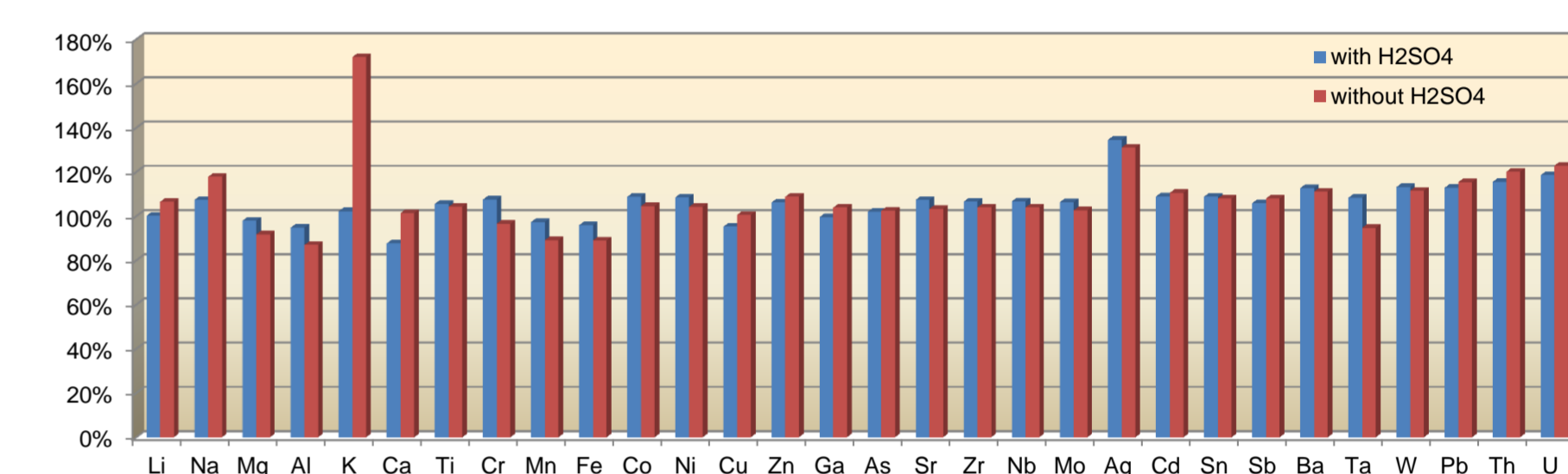
Results and Discussion

13 PV Si samples were collected from various countries and analyzed. Results of typical elements are shown below.



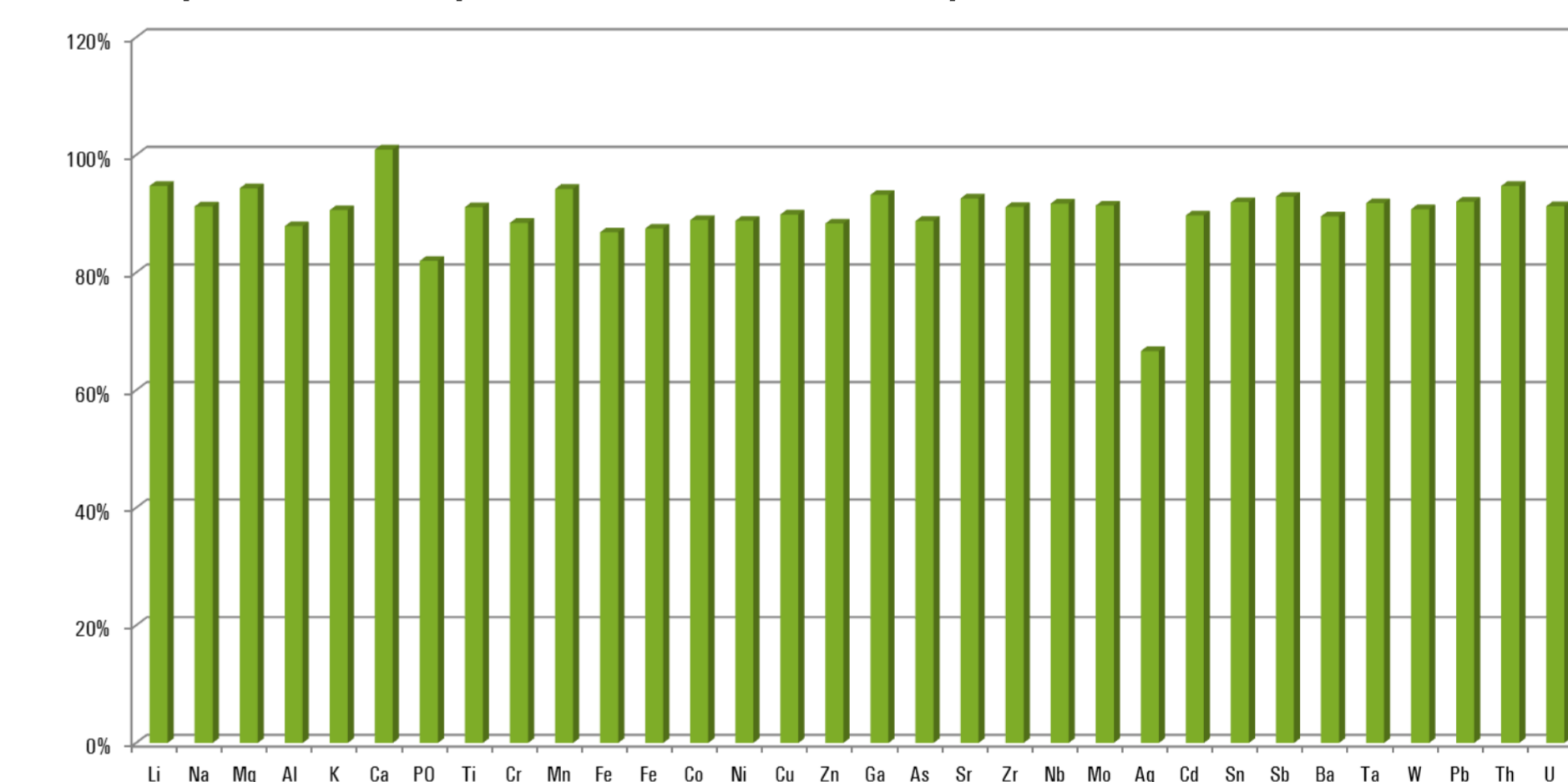
To verify the analytical result, a recovery test was carried out. PV Si solution before heating was divided into 2 groups. Aliquot of standard solution was added to one group so that the final spike concentration became 5ppb. Recovery rate was calculated by comparing spiked and non spiked data.

	prep blank	with H ₂ SO ₄			without H ₂ SO ₄			
		unspiked	spiked	recovery	unspiked	spiked	recovery	
¹¹ B		0.0051	0.026	0.086	1%	0.070	5.00	99%
³¹ P ¹⁶ O		0.11	0.055	4.2	84%	46	190	3000%
²⁸ Si		0.11	0.41	0.00		13000	25000	



Si remaining in solution is less than 1ppb when H₂SO₄ is added while no H₂SO₄ solution contains 20 to 30ppm Si.

Assuming that PV Si wafer is homogenous, standard solution was also spiked to Si pieces. The recovery test result is shown below.

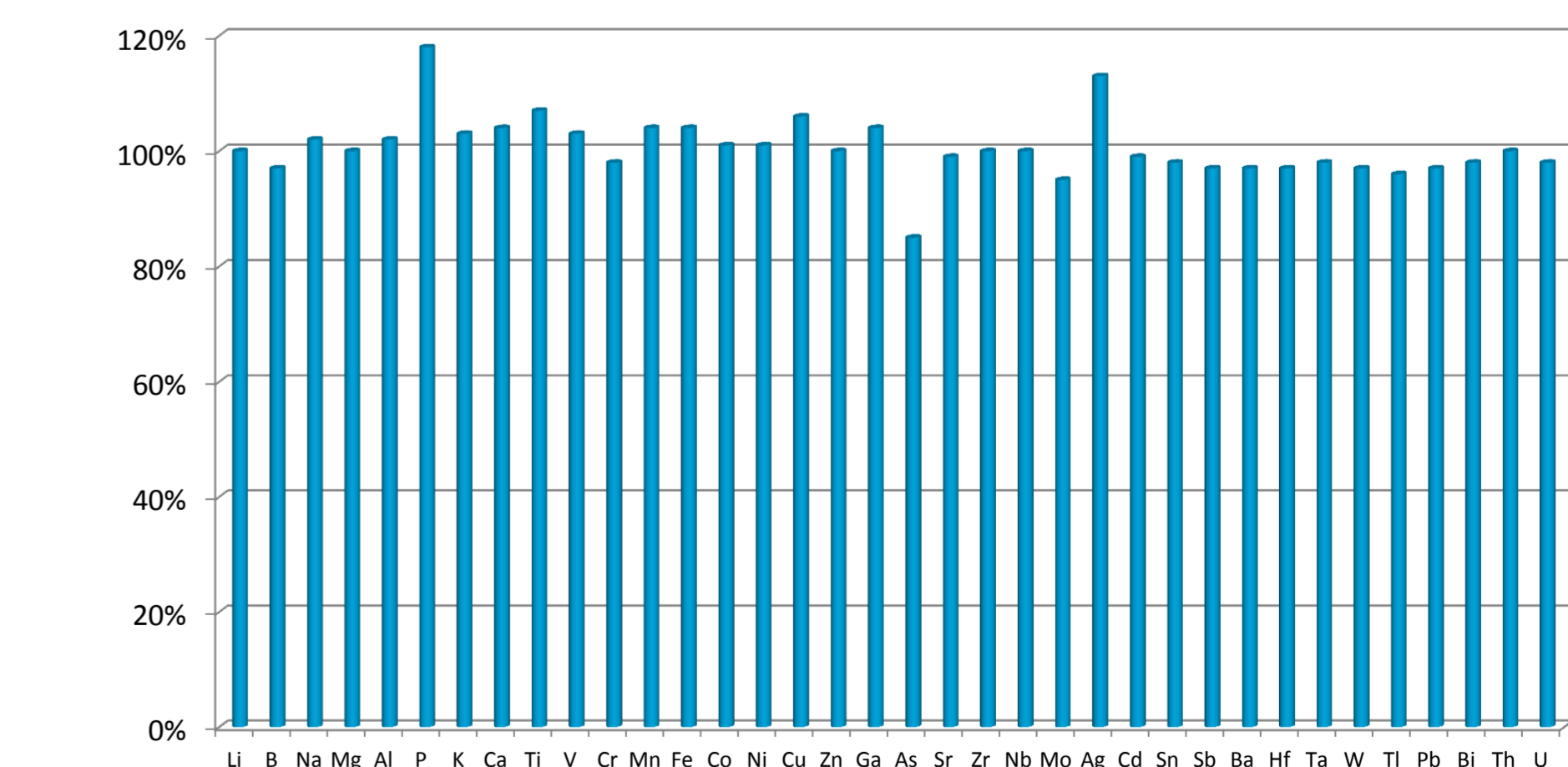


Ag shows poor recovery. The source is under investigation.

2 TCS sample were analyzed. Sample A was transported in a glass vial and B was in a stainless container. Analytical result is below. (ppb)

	Sample A	Sample B	Sample A	Sample B	
Li	0.00	0.00	As	0.14	0.00
B	1.4	5.5	Sr	0.01	0.1
Na	0.53	15	Zr	0.08	1.0
Mg	2.5	1.4	Nb	0.00	0.00
Al	0.75	8.5	Mo	0.08	1.3
P	2.7	4.2	Pd	0.00	0.00
K	0.23	3.6	Ag	0.03	0.00
Ca	0.83	26	Cd	0.00	0.00
Ti	0.08	2.3	Sn	0.38	1.7
V	0.08	0.6	Sb	0.08	0.5
Cr	0.12	22	Ba	0.00	1.4
Mn	0.01	1.6	Ta	0.00	0.2
Fe	1.9	180	W	0.00	0.3
Co	0.0	0.3	Au	0.00	0.00
Ni	0.08	18	Pb	0.00	0.8
Cu	0.08	0.8	Th	0.00	0.00
Zn	0.38	3.5	U	0.00	0.00
Ga	0.01	0.00			

Serious contamination can be found in sample B due to corrosion of stainless steel. The recovery test result is shown below.



Conclusion

Analytical method of solar cell material has been established not only for ICP-MS tuning (cool plasma, high energy collision) but also for sample preparation. Proper sample preparation enables detection of impurities below 1ppb by Agilent 7700s ICP-MS.

For safety reasons a stainless container is used for transportation of TCS. Plastic or glass containers can be used if analytical lab is located close to sampling point.