Improved Detection of Trace Elements in a Silicon Matrix Using a Desolvating Nebulizer System with ICP-MS

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Abstract:

Inductively coupled plasma mass spectrometry (ICP-MS) can routinely provide single digit and sub-ppt detection limits for many elements. Since trace element impurities in the silicon used for solar panels can adversely affect the efficiency of panel operation, ICP-MS is commonly used for this application.

This paper will describe the use of a reaction-cell quadrupole ICP-MS with a desolvating nebulizer system for detection of trace elements in a Si matrix up to 5000 mg/L. The nebulizer system uses a PFA nebulizer / spray chamber with a fluoropolymer membrane desolvator for best resistance to a sample acid matrix of 3 to 5% HF/HNO_3 or 3 to 5% H_2O_2. Analyte elements of interest include Ti, V, Fe, and Mo.

Operating conditions of the reaction cell ICP-MS and the desolvating nebulizer system will be described. Figures of merit will include enhanced analyte signal, reduced silicon matrix effects, and analyte recoveries with a high concentration of silicon.

Instrumentation

ICP-MS: PerkinElmer DRCII
ICP-AES: PerkinElmer Optima 7300DV

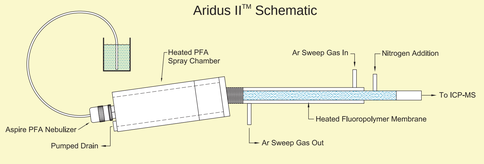
Desolvating Nebulizer System: CETAC Aridus II

Low-Flow PFA Nebulizers:

CETAC Aspire-100 (100 µL/min)
ESI PFA-100 (100 µL/min)
ESI PFA-20 (20 µL/min)

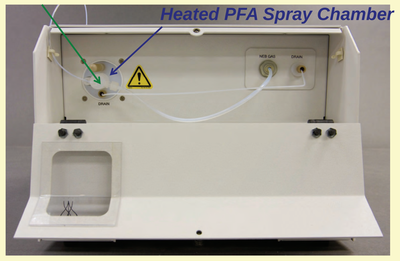
Note: Aridus II PFA spray chamber can accept standard 6mm diameter concentric nebulizers with flow rates up to 200 µL/min.

CETAC Aridus II Desolvating Nebulizer System

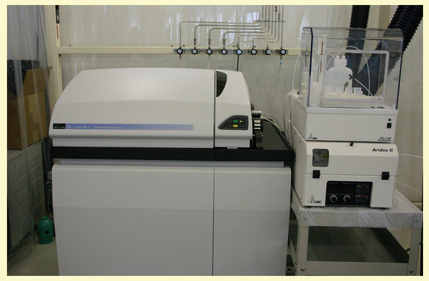


CETAC Aridus II Schematic

Aspire PFA Nebulizer



CETAC Aridus II – Front Door Open



PerkinElmer ELAN DRCII ICP-MS w. CETAC Aridus II and ASX-112FR Autosampler

Operating Conditions - I

ICP-MS:	PerkinElmer ELAN DRCII
Nebulizers:	Aspire-100, PFA-20 & PFA-100
Spray Chamber:	Glass cyclonic
ICP Power:	1600 W
Plasma Gas:	18 L/min
Auxiliary Gas:	1.2 L/min
Nebulizer Gas:	1.15 L/min (PFA-20) 1.12 L/min (PFA-100)
Dwell time:	50 milliseconds
Sweeps/reading:	20
Readings/replicate:	1
Replicates:	3

Operating Conditions - II

Desolvating Nebulizer System:	CETAC Aridus II
Nebulizer Gas (from ICP-MS):	0.90 L/min (PFA-20) 0.90 L/min (Aspire-100)
Spray Chamber Temp:	110°C
Membrane Oven Temp:	160°C
Ar Sweep Gas Flow:	7.1 L/min (PFA-20) 6.5 L/min (Aspire-100)
N_2 Addition Gas:	4 mL/min (both nebulizers)

Sensitivity Comparison - I

Element	m/z	Cyclonic w. PFA-20 (cps)	Aridus II w. PFA-20 (cps)	Factor
Mg	24	5460	18700	3.4
In	115	20530	51750	2.5
Ba	138	17990	43530	2.4
Ce	140	19490	39800	2.0
U	238	17470	35950	2.0

1µg/L Tuning Solution

Sensitivity Comparison - II

Element	m/z	Cyclonic w. PFA-100 (cps)	Aridus II w. Aspire-100 (cps)	Factor
Mg	24	14060	101730	7.2
In	115	53990	404110	7.4
Ba	138	47160	290400	6.1
Ce	140	52730	332300	6.3
U	238	44840	335900	7.4

1µg/L Tuning Solution

Sample Preparation Procedure

Silicon matrix solution prepared from a Si wafer:

1. Wash wafer with 18 Mohm deionized water.
2. Remove a ~2 gram section of the wafer.
3. Wash wafer section with 1% high-purity HNO_3.
4. Add 68% HNO_3 and 38% HF to wafer section and dissolve.
5. Dilute resulting solution to 5% HF.
6. Measure Si concentration by ICP-MS (ELAN DRCII) and ICP-AES (PerkinElmer Optima 7300DV)

Note: HNO_3 and HF were Tamapure AA100 grade (Tama Chemicals, Kawasaki City, Kanagawa Japan).

Operating Conditions - III

ICP-MS:	PerkinElmer ELAN DRCII
ICP Power:	1600 W
Plasma Gas:	18 L/min
Auxiliary Gas:	1.2 L/min
Nebulizer Gas:	0.9 L/min
Reaction Gas:	NH_3
Desolvation System:	CETAC Aridus II w. PFA-20
Spray Chamber Temp:	110°C
Membrane Oven Temp:	110°C
Ar Sweep Gas Flow:	8.3 L/min
N_2 Addition Gas:	4 mL/min

Recovery Experiment

1. Dilute the prepared Si matrix solution to concentrations up to 5000 mg/L.
2. Prepare both non-spiked and spiked (2 µg/L) Si matrix solutions.
3. Calibrate ICP-MS with multielement standard solution (0 mg/L Si) and measure recoveries for spiked Si matrix solutions.

Recoveries in Silicon Matrix

Analyte	m/z	DRC Mode	200 mg/L Si	500 mg/L Si	1000 mg/L Si	2000 mg/L Si	5000 mg/L Si
Na	23	Std	123	>130	>130	>130	89
Mg	24	Std	113	108	128	>130	108
Al	27	DRC	103	109	112	95	95
K	39	DRC	124	>130	>130	>130	109
Ca	40	DRC	121	>130	>130	107	107
Ti	48	DRC	111	96	112	106	115
V	51	DRC	82	97	89	86	95
Cr	52	DRC	123	121	122	121	120
Fe	56	DRC	108	129	>130	121	111
Ni	60	DRC	120	123	124	122	114
Cu	63	DRC	114	110	111	112	114
Zn	66	DRC	119	128	118	111	96
Ga	69	DRC	121	120	120	116	109
As	75	DRC	123	103	129	90	111
Sr	88	Std	114	115	121	120	116
Zr	90	Std	116	115	123	120	115
Mo	95	Std	104	110	108	110	102
Cd	114	Std	114	115	117	112	102
Sn	118	Std	116	117	121	117	110
Sb	123	Std	115	112	114	104	89
Ba	138	Std	115	116	122	118	116
W	184	Std	115	117	122	120	116
Pb	208	Std	113	115	120	120	113

Notes: Recoveries are given in %; values > 130% are all < 200% and may indicate sample contamination.
Std = standard mode, no NH_3 gas
DRC = dynamic reaction cell mode with NH_3 gas

Summary:

1. A desolvating nebulizer system with nitrogen gas addition can significantly enhance analyte signal with reaction-cell based quadrupole ICP-MS, depending on solution uptake rate. A 20 µL/min PFA nebulizer provided a factor of 2 to 3 fold signal enhancement while a 100 µL/min PFA nebulizer provided a 6 to 7 fold improvement.
2. The 20 µL/min PFA nebulizer provided the best performance for higher Si matrix concentrations up to 5000 mg/L, with lower Si matrix loading to the ICP-MS and consistent overall analyte recoveries.