DIRECT ANALYSIS OF UNDILUTED PHOTORESIST WITH INLINE AUTODILUTION INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

Hyun-Kee Hong[1], J. S. Lee[2], Austin Schultz[2], Paul Field[2] and Daniel Wiederin[2]
[1]Samsung Electronics Co., Ltd., South Korea
[2]Elemental Scientific Inc., USA (lee@icpms.com)

Introduction

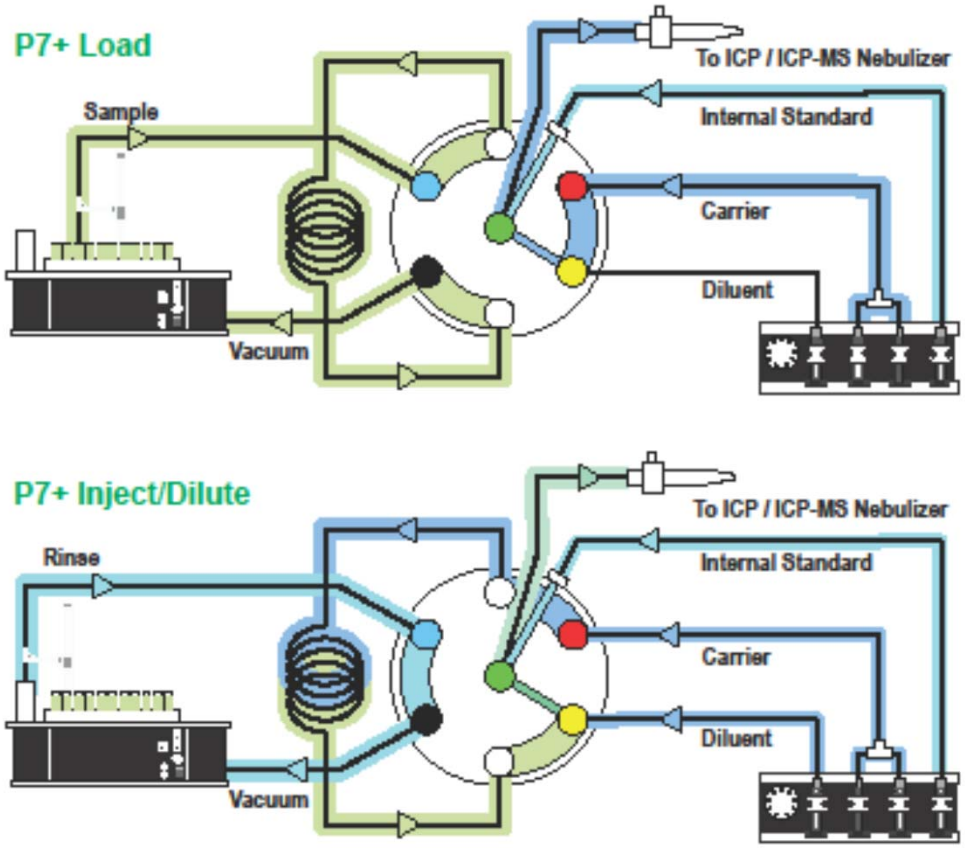
This presentation discusses a fully automated method to analyze metal contaminants in undiluted photoresist using ICPMS and a new inline dilution system called prepFAST.

prepFAST is a fully-automated inline sample and standard autodilution system consisting of a syringe pump unit (S400V), an 8-port inline mixing valve and an autosampler. The sample is loaded from the autosampler into a loop on the valve. After the valve moves to the inject position, a syringe-driven solvent carrier stream pushes the sample out of the loop where it is mixed inline and in-valve with syringe-driven diluent and internal standard streams before introduction to the ICPMS nebulizer. The flow rates are precisely and variably controlled at rates between 1 and 500 µL min^{-1}. With prepFAST ICPMS, it is possible to introduce and analyze undiluted photoresist samples.

Because the samples are automatically diluted inline by the prescribed dilution factor, the difficult and contamination-prone off-line dilution step is avoided. The valve system also minimizes the amount of sample introduced to the ICPMS, improving long-term instrument stability. This real time dilution feature of prepFAST ICPMS reduces reagent consumption, lowers contamination risks, minimizes ICPMS maintenance and minimizes human exposure to hazardous chemicals. This presentation evaluates and discusses inline dilution and analysis of photoresist in terms of linearity, precision, accuracy and stability.

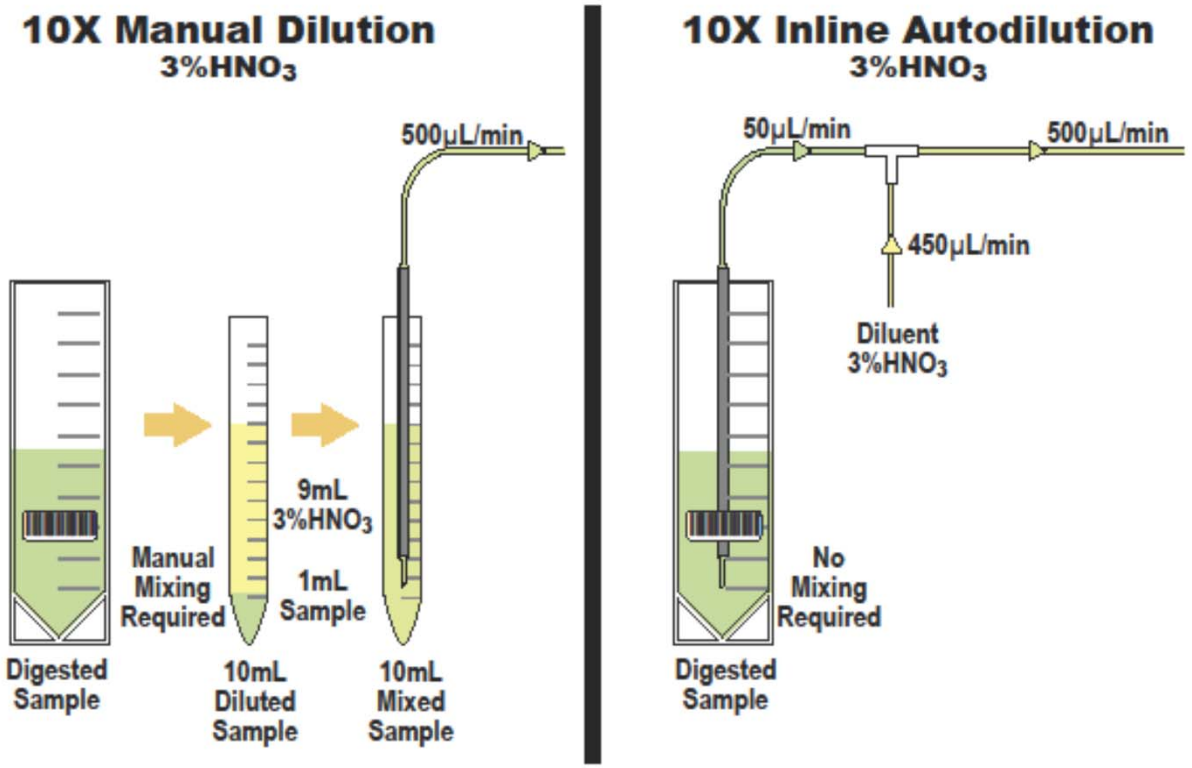
prepFAST Inline Autodilution System

Load, Inject, Dilute and Analyze



prepFAST Inline Autodilution System

Manual Dilution vs Inline Autodilution

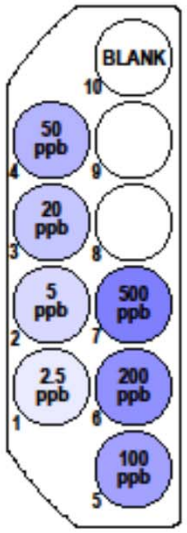


prepFAST Inline Autodilution System

Conventional Calibration vs prep*FAST* Autocalibration

Conventional Calibration
(seven points)

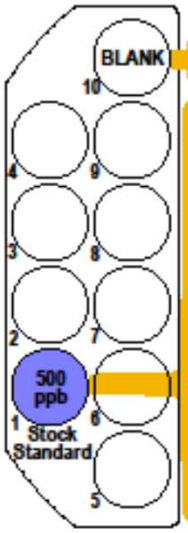
Offline Prep: 1 Blank + 7 Standards



STD Position	Concentration
10	0
1	2.5
2	5
3	20
4	50
5	100
6	200
7	500

prepFAST Autocalibration
(seven points)

Inline Prep: 1 Blank + 1 Standard

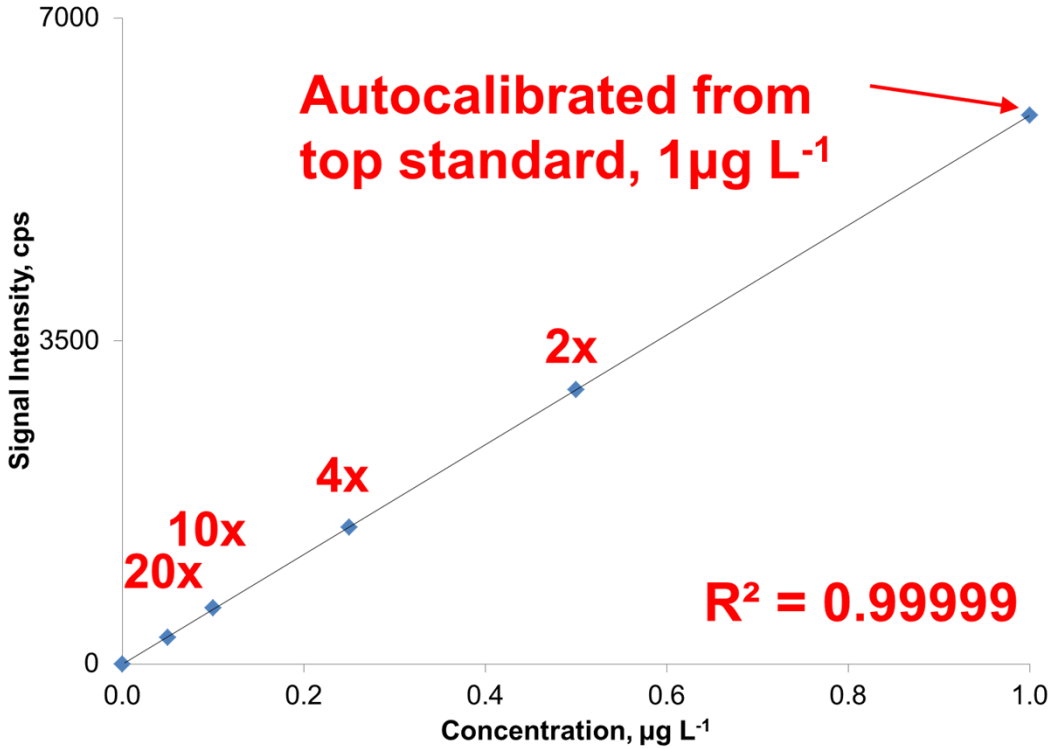


STD Position	Inline Dilution Factor	Flow Rate (µL/min) Std	Diluent	Total	Concentration
10	200x	2.5	497.5	500	0
1	200x	2.5	497.5	500	2.5
1	100x	5	495	500	5
1	40x	20	487.5	500	20
1	10x	50	450	500	50
1	5x	100	400	500	100
1	2.5x	200	300	500	200
1	1x	500	0	500	500

prep*FAST* Calibration: Blank can be analyzed diluted or undiluted.

Autocalibration

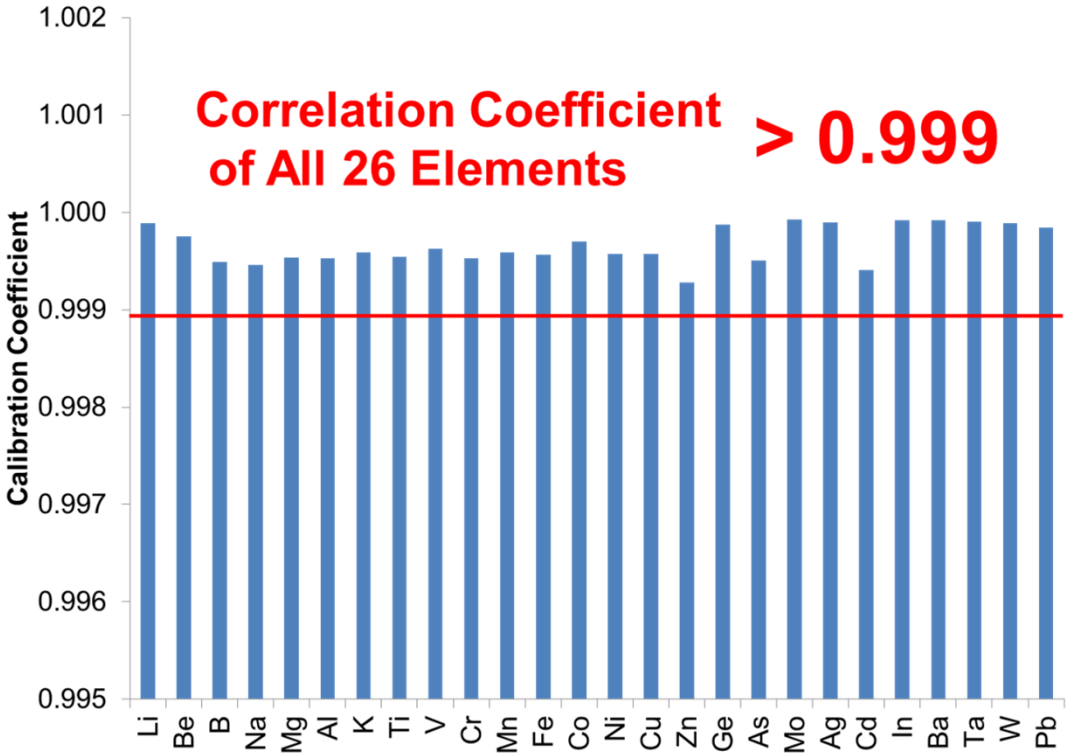
Cr Calibration



User predefined dilution factors for a single multi-element standard of 1 µg L^{-1} in N-methyl-2-pyrrolidon are used to build calibration curves. Accuracy of dilution is illustrated by excellent linearity of the calibration curve (R^2 = 0.99999).

Autocalibration

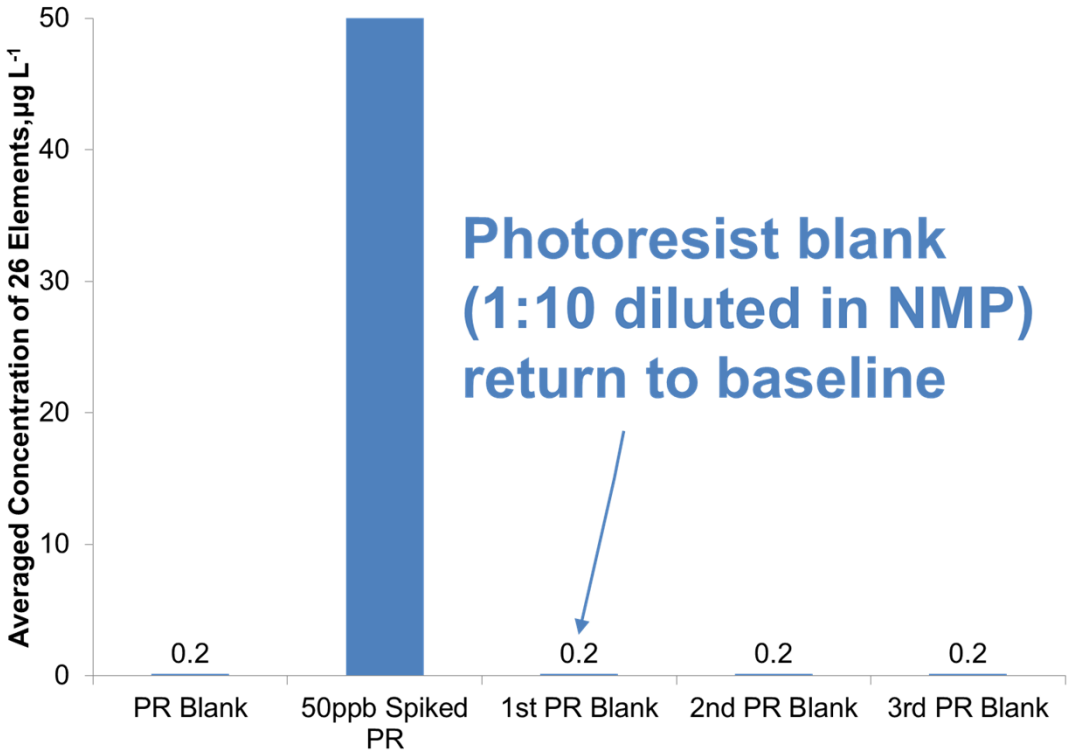
Linearity of Autocalibration



Twenty six potential contaminant elements in N-methyl-2-pyrrolidon were auto-calibrated from a single 1 µg L^{-1} multielement standard solution. Autocalibration replicated 10 times and the averaged correlation coefficient of all elements exhibit better than 0.999 R^2 valvue.

Washout

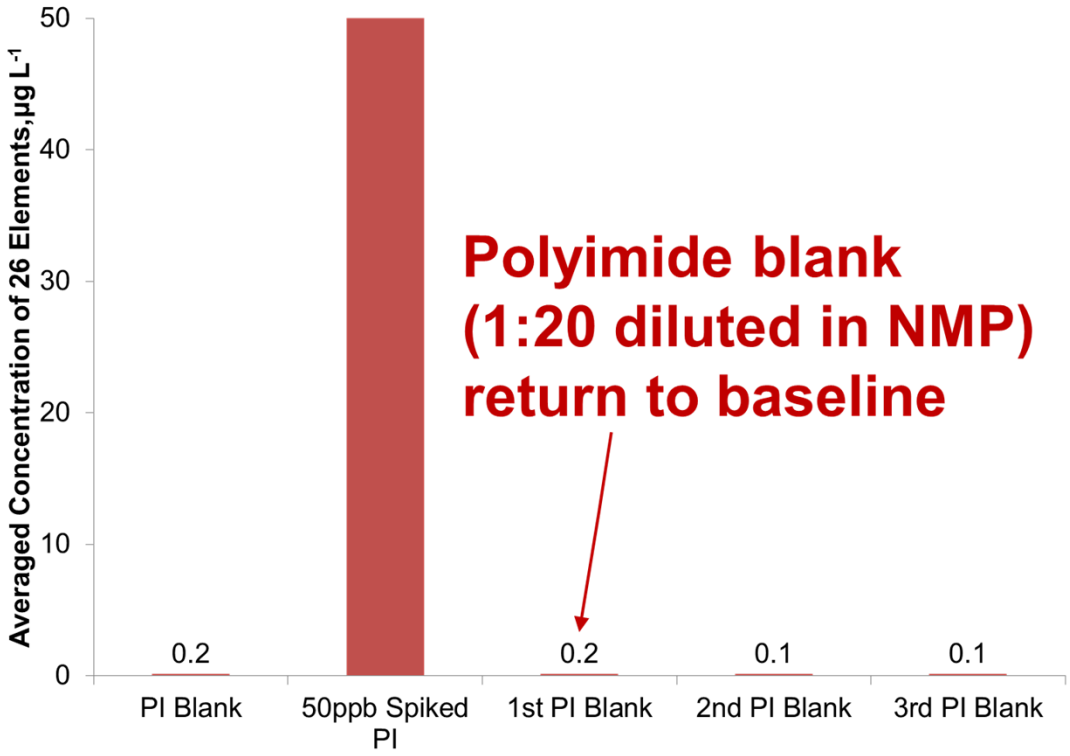
Photoresist



The blank concentration level in photoresist goes back to the previous baseline level at the fist blank after 50 µg L^{-1} spiked photoresist analysis with prepFAST system. (Eements; Li, Be, B, Na, Mg, Al, K, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ge, As, Mo, Ag, Cd, In, Ba, Ta, W and Pb)

Washout

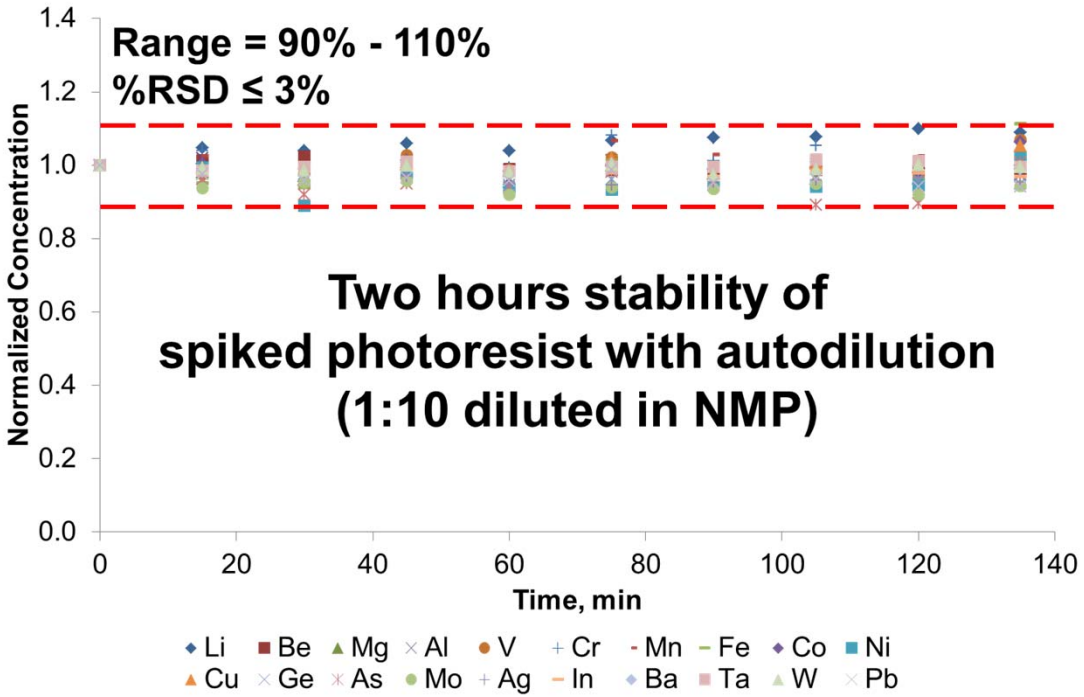
Polyimide



The blank concentration level in polyimide goes back to the previous baseline level at the fist blank after 50 µg L^{-1} spiked polyimide analysis with prepFAST system. (Eements; Li, Be, B, Na, Mg, Al, K, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ge, As, Mo, Ag, Cd, In, Ba, Ta, W and Pb)

Stability

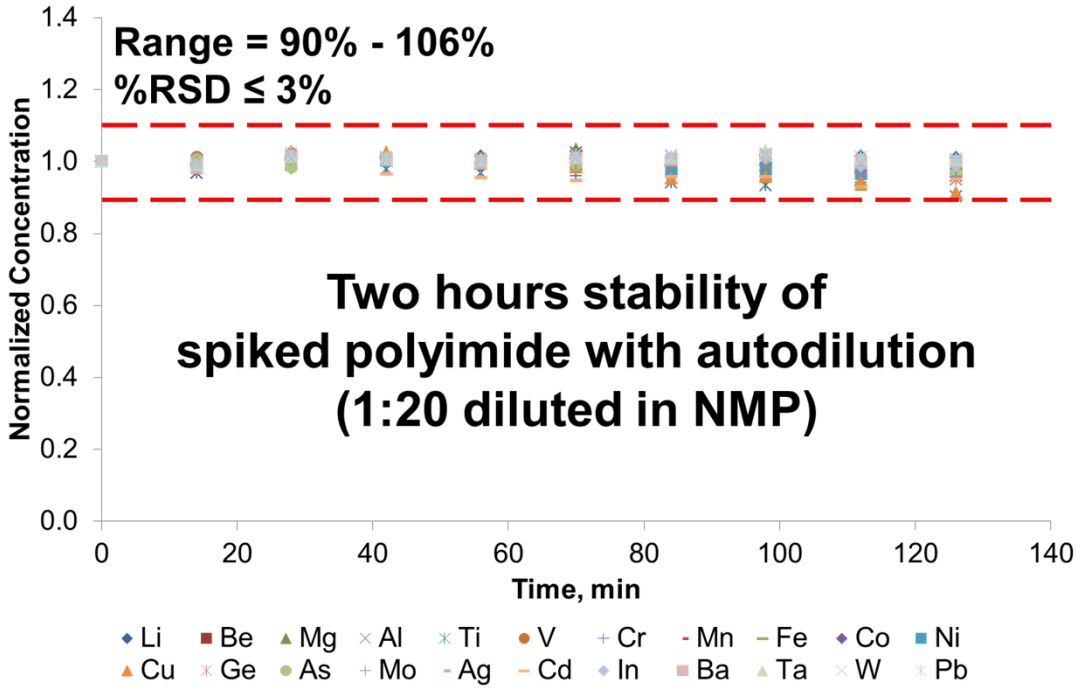
Photoresist



Two hours stability is plotted for a 10 fold inline auto dilution of spiked photoresist. These data indicates that undiluted photoresist can simple be placed in a tube and diluted inline to appropriate TDS for ICPMS analysis.

Stability

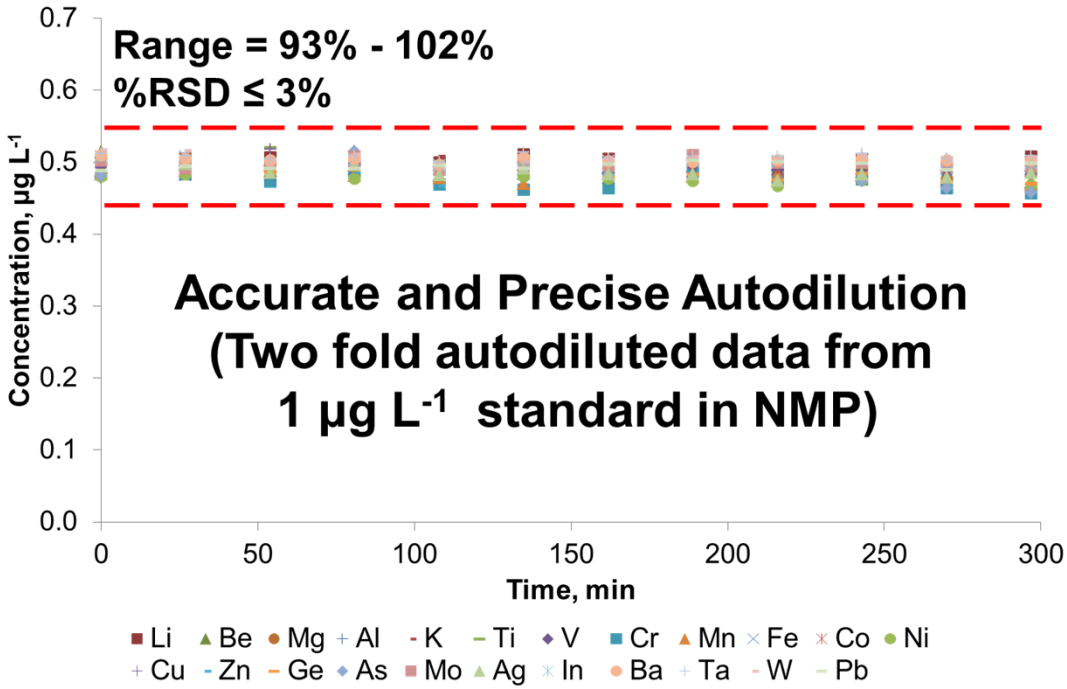
Polyimide



Two hours stability is plotted for a 5 fold inline auto dilution of 4 fold manually diluted and spiked polyimide.

Accuracy & Precision

N-methyl-2-pyrrolidone



Twelve replicate analysis of a 2 fold auto dilution of 1 µg L^{-1} in N-methyl-2-pyrrolidone ran over an 5 hours period demonstrate accuracy and precision of both standardization and replicate analysis. The signal stability was less than 3% and the accuracy was less than 10% for all elements during the period in spite of the complex organic matrix.

Limit of Detection

Table of Detection Limit (unit: ng L^{-1})

Element	N-methyl-2-pyrrolidone	Photoresist (1:10 in NMP)	Polyimide (1:20 in NMP)
Li (7)	0.8	2	8
Be (9)	0.5	0.5	0.4
B (11)	38	45	61
Na (23)	54	66	515
Mg (24)	43	8	26
Al (27)	34	8	18
K (39)	25	55	33
Ti (48)	6	76	126
V (51)	6	5	16
Cr (52)	4	4	33
Mn (55)	1	1	3
Fe (56)	14	21	59
Co (59)	0.3	0.5	1
Ni (60)	20	9	19
Cu (63)	23	22	62
Zn (66)	30	29	70
Ge (74)	5	3	71
As (75)	6	5	4
Mo (95)	10	9	32
Ag (107)	0.5	0.4	3
Cd (111)	3	3	6
In (115)	0.07	0.07	0.1
Ba (138)	0.2	0.5	0.5
Ta (181)	0.5	0.3	1
W (184)	0.6	0.6	1
Pb (208)	0.8	2	2

This table shows the limit of detections (LOD) for N-methyl-2-pyrrolidone, 1:10 diluted photoresist and 1:20 diluted polyimide samples by prepFAST ICPMS. LODs were calculated using three times of the standard deviation (n = 10) of the sample divided by thel slope of N-methyl-2-pyrrolidone calibration curve.

Conclusion

The prepFAST system permits direct analysis of undiluted photoresist samples with precise and accurate results.

The prepFAST performs inline auto calibration, auto dilution, and eliminating the majority of sample preparation and lowers contamination risks for ICPMS. It offers excellent short and long-term precision, accuracy at any dilution factor, and improved throughput and washout compared to standard sample introduction even in the complex organic matrix samples.