Precision and Accuracy of Online Autodilution Using ISIS (Integrated Sample Introduction System)

Technical Note

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Introduction

ICP-MS has been used throughout the semiconductor industry as a trace element analyzer capable of measuring ultra-low concentrations at sub-ppt levels.

More recently, ICP-MS has attracted considerable attention as the analytical method of choice for the measurement of metal elements in potable and industrial waters. This is due to its ability to simultaneously measure a large number of analytes over a linear dynamic range of up to 8 decades.

In combination with various alternative sample introduction systems, the range of ICP-MS applications can be increased further.

The 7500 ICP-MS Series Integrated Sample Introduction System (ISIS) is one of such alternative sample introduction system, enabling various functions such as on-line dilution, higher sample throughput and discrete sampling analysis. This technical note focuses on its on-line dilution capability.

By utilizing ISIS with the optional 7500 ICP-MS intelligent sequencing software, samples beyond the measurable concentration range (beyond the upper calibration limit) are automatically diluted and measured again without intervention.

Increasing the dynamic range an additional factor of 10-20x

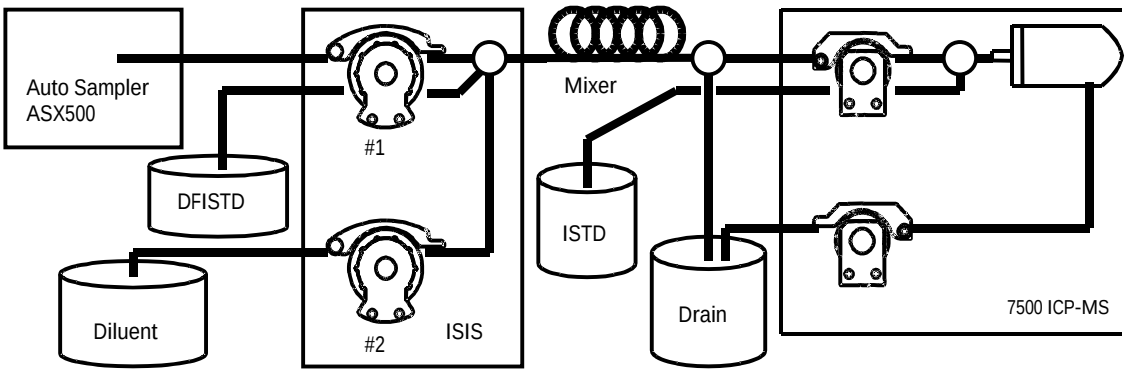

Figure 1
Auto Dilution System Sketch of the ISIS

allows samples outside the normal concentration range to be measured automatically.

Overview of ISIS Auto Dilution

ISIS is equipped with two, three-channel peristaltic pumps. Dilution is automatically achieved by changing the ratio of flow rate of sample and diluent. The flow diagram is shown in Figure 1.

Samples loaded in the ASX500 autosampler are delivered to pump #1 along with the dilution factor internal standard (DFISTD) for dilution factor correction. The diluent is added by pump #2 and the diluted sample is mixed by the mixer before splitting the surplus flow to the drain.

Finally, the quantitative internal standard (ISTD) is added to the samples by the 7500 ICP-MS on-board pump which are introduced to the nebulizer at constant flow.

ISIS supports autodilution factors of 5, 10 and 20X by volume. The relative speed of the two pumps changes depending on dilution factor selected.

Though the ISIS pumps are exceptionally stable and free from pulsation, ISIS uses one of two correction modes compensate for tubing fatigue and variations in tubing inner diameter.

The first correction mode (Periodic mode) calculates the actual dilution factor by measuring a dilution factor check standard periodically. The second mode (Simultaneous mode) calculates the dilution factor for each sample by measuring the dilution factor internal standard (DFISTD) in each sample both before and after dilution. The calculated dilution factor is used to accurately and precisely correct the concentration of original sample. Final concentration is corrected for both prep dilution and autodilution.

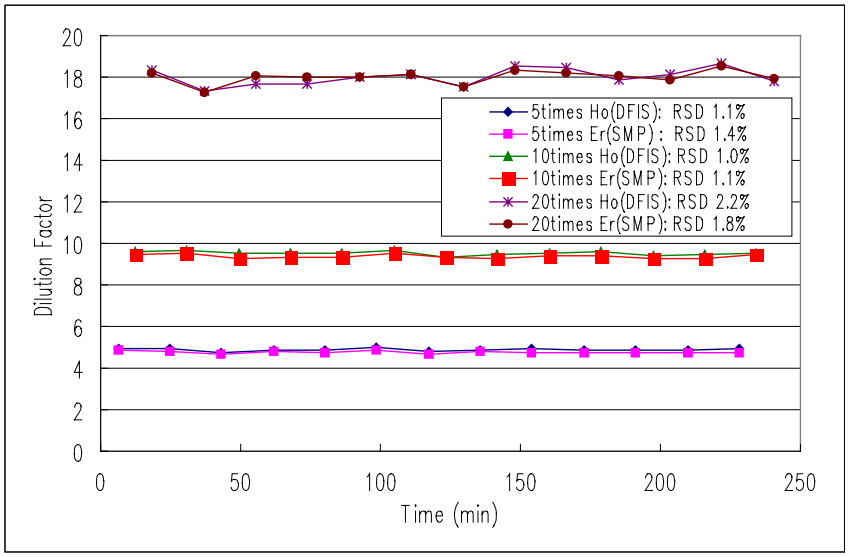

Figure 2
Dilution Factor Reproducibility (4 Hours)

Table 1 Result of the Quantitative Analysis

	Y	Ce	Tl
Internal Standard	In	In	Bi
Mean quantitative value (ppb)	101	102	100
Reproducibility (RSD%)	1.7	1.8	1.6

Dilution Performance

ISIS showed excellent accuracy and precision of dilution in simultaneous mode for actual samples (drinking water).

Samples containing 100 ppb of Y, Ce, Tl and Er were measured for four hours alternately diluted and non-diluted.

In this dilution experiment, the dilution factor varied from 5, 10 to 20 times as follows:

No dilution .5 times . no dilution .10 times . no dilution .20 times... (Simultaneous mode). Ho was used as DFISTD.

To verify the appropriatness of DFISTD (DFISTD behaves the same as samples do), the reproducibility of both Ho and Er which have similar masses and chemical characteristics, is shown in Figure 2.

The reproducibility of the 5, 10 and 20x dilutions was very good, with %RSDs less than 2%.

Because Er (sample) and Ho (DFISTD) were observed to behave similarly, the ratio of sample and DFISTD introduced was determined to be constant. Therefore, the dilution factor of the sample can be calculated by monitoring the DFISTD.

The quantitative result for Y, Ce, and Tl calculated using the simultaneous mode dilution factor (DFISTD) is shown in Table 1 and Figure 3.

The results were very good: deviation of the quantitative mean value from the true value was within 2% and %RSD was less than 2%.

Measuring Tap Water by Automatic Dilution with Intelligent Sequencing

By utilizing ISIS and Intelligent Sequencing in combination, Samples outside a preset concentration range are automatically diluted and measured again.

Figure 4 depicts the experimental protocol including samples whose concentration exceeded the upper calibration range and were automatically diluted and re-measured.

The calibration ranges were determined by adopting water quality reference values defined in the Waterworks Law in Japan as the upper calibration limit. Samples beyond that upper limit were automatically diluted 10x and re-measured.

Normal tap water and tap water spiked at twice the regulated concentration for Na, Al, Cu and

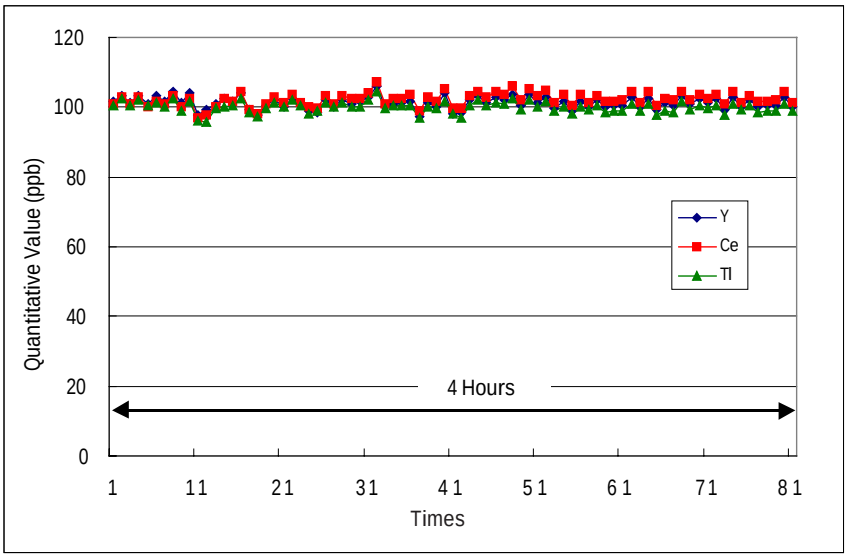

Figure 3
Quantitative Reproducibility (4 Hours)

Table 2 Operating Conditions for Tap Water Analysis

RF Power:	1.5 kW
Sampling depth:	9 mm
Carrier Gas Flow:	1.12 L/min
Sample Flow:	500 mL/min
Nebulizer:	Babington type
DFISTD:	Ho 500ppb
ISTD:	Co, Tb, Bi 500ppb (Tb is used to correct the response for Ho.)
Diluent:	2% Nitric Acid

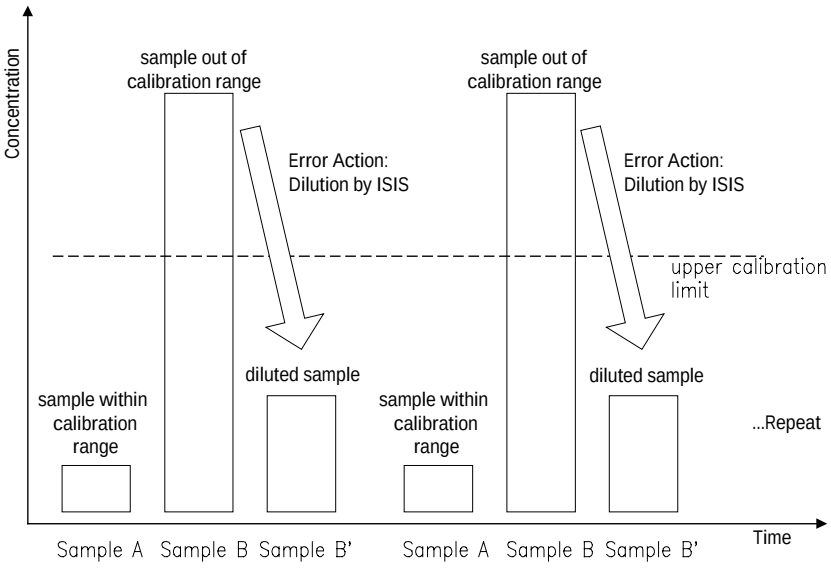

Figure 2.
Pb calibration plot

Table 3 Result of Tap Water Recovery

Element	Mass Number	Internal Standard (Mass #)	Quantitative Value (non-addition)*	Quantitative Value (addition)*	Addition amount	Recovery	Reproducibility (4 Hours)
Na	23	Co (59)	14.96 ppm	413.2 ppm	400 ppm	100 %	1.2 %
Al	27	Co (59)	3.86 ppb	413.9 ppb	400 ppb	103 %	1.3 %
Cu	65	Co (59)	5.05 ppb	1994 ppb	2 ppm	99 %	1.1 %
Pb	208	Bi (209)	0.77 ppb	100.5 ppb	100 ppb	100 %	1.2 %

* These values are original concentration.

Pb were analyzed for 4 hours.

The recoveries for each spiked element of this study are shown in Figure 5.

Table 3 indicates the quantitative results for four elements in the unspiked tap water, the spiked tap water, the spike recoveries and %RSD.

The recoveries of the measured four elements ranged from 99% to 103%. Recovery precision over 4 hours was better than 2%.

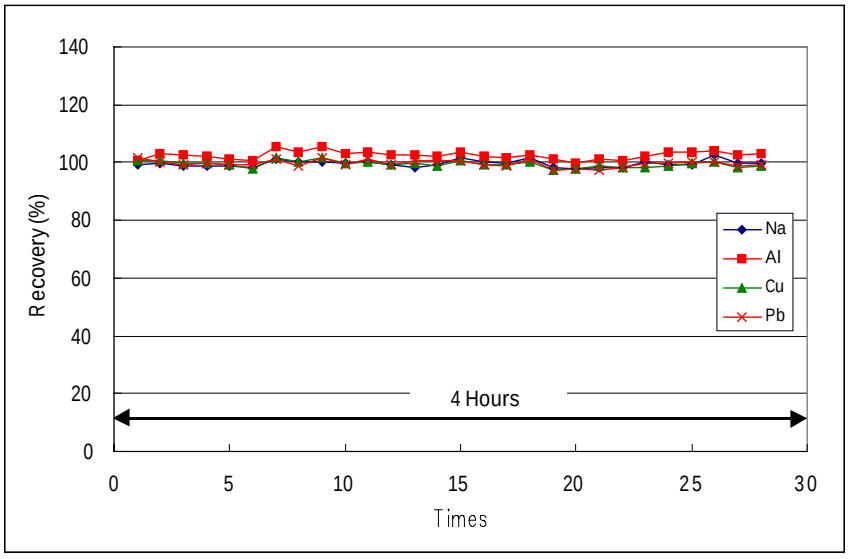

Figure 5
Trend of the Tap Water Recovery (4 Hours)

Conclusion

ISIS, in combination with Intelligent Sequencing can be used to automatically dilute and re-measure samples whose concentration exceeds a preset value. Since dilution is automatically executed as needed, sequence setup is fundamentally the same as the standard system without autodilution.

However, if the necessity of dilution is known before analysis, it is also possible to instruct the system to dilute all samples. This reduces the matrix load on the ICP and mass spectrometer components when known high matrix samples are to be introduced.

Since ISIS is operated online and in real time for dilution, analysis time is significantly reduced compared to discrete-type autodiluters and no additional autosampler positions are used for the diluted samples.

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Printed 7/2003
Publication number 5968-6493E

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