ANALYTICAL SCIENCE & TECHNOLOGY
(*Journal of the Korean Society of Analytical Sciences*)
Vol. 8, No. 4, 1995
Printed in the Republic of Korea

Determination of Li by Isotope Dilution Inductively Coupled Plasma Mass Spectrometry

Chang J. Park
Korea Research Institute of Standards and Science,
P.O. Box 102, Yusung, Taejon, 305-600, Korea

Bag S. Chung
Research Ceter, Korea Electric Power Corporation,
Yusung-Gu, Taejon, 305-380, Korea

Abstract : Inductively coupled plasma mass spectrometry combined with the isotope dilution method is used for the determination of lithium. The isotope dilution method is based on the addition of a known amount of enriched isotope (spike) to a sample. The analyte concentration is obtained by measuring the altered isotope ratio. The spike solution is calibrated through so called reverse isotope dilution with a primary standard. The spike calibration is an important step to minimize error in the determined concentration. It has been found essential to add spike to a sample and the primary standard so that the two isotope ratios should be as close as possible.
Since lithium is neither corrosive nor toxic, lithium is used as a chemical tracer in the nuclear power plants to measure feedwater flow rate. 99.9% ^{7}Li was injected into a feedwater line of an experimental system and sample were taken downstream to be spiked with 95% ^{6}Li for the isotope dilution measurements. Effects of uncertainties in the spike enrichment and isotope ratio measurement error at various spike-to-sample ratios are presented together with the flow rate measurement results in comparison with a vortex flow meter.

Key words : ICP-MS, isotope dilution, lithium, chemical tracer, flow rate

1. Introduction

Lithium is one of important elements determined in clinical laboratories because lithium is a therapeutic agent for manic-depressive illnesses.[1] Lithium is also one of the elements controlled in semiconductor process chemicals. For example, lithium should be controlled to below 10 ppt for the process chemicals used in 1 M DRAM.[2] It is perhaps unfamiliar to most analytical chemists that analytical measurements of Li are used for an engineering application. In nuclear power plants, accurate measurement of feedwater flow rate is very important for both safety and maximum power generation. The feedwater flow rate is generally obtained by the measurement of pressure difference across a venturi. However, this measurement sometimes gives inaccurate flow rates due to corrosion fouling, and a poorly-developed velocity profile.[3] Thus, in order to correctly estimate the reactor thermal power, the feedwater flow rate is independently measured using a chemical tracer method. As a chemical tracer, lithium is used because lithium is neither radioactive nor corrosive.

In such an apllication, an analytical method is required which provides both high accuracy and high sample throughput. This is because lithium concentration of the feedwater sample is required to be determined with an uncertainty less than 0.2%.

Such a high degree of accuracy and sample throughput can be achieved by the isotope dilution method combined with inductively coupled plasma mass spectrometry(ICP-MS). In the isotope dilution method, the spike isotope is calibrated through reverse isotope dilution with the primary standard. The reverse isotope dilution is an important and integral part of the isotope dilution process, making potential systematic errors cancelled or minimized in the final result as long as the conditions of isotope ratio measurements are consistent.[4]

This paper shows how the reverse isotope dilution process can be applied and why the process is necessary to minimize systematic error due to spike enrichment uncertainty. The whole isotope dilution procedure has been optimized for an accurate determination of lithium and the result was applied to the flow rate measurements.

2. Experimental

2.1 Enriched Isotopes and Reagents

Enriched ^{6}Li (95%) metal was obtained from US Services Inc.(Summit, NJ, USA) and enriched $^{7}LiOH$ (99.9%) was purchased from Oak Ridge National Laboratory (Oak Ridge, TN, USA). The ^{6}Li metal, originally stored with oil in a bottle by the vendor, was cleaned with acetone inside an argon-filled drying box before dissolution. An appropriate amounts of the enriched isotopes were dissolved in deionized water. All the prepared solutions were acidified to 1% nitric acid (w/w) with ultrapure nitric acid (Dong Woo Chemical Ltd., Korea).

2.2 Instrumentation

The ICP-MS instrument employed in this work is a laboratory-built unit. Instrument components and operating conditions are listed in Table 1. For sample introduction, a Meinhard concentric nebuliser (TR-30-C1) and Scott-type spray chamber were used, and a peristaltic pump (Minipuls3, Gilson) to control the sample uptake rate. An off-axis ion lens was used in this instrument where its quadrupole and interface centers were 8 mm apart. Ions exiting the quadrupole filter are 90° deflected into the mouth of a discrete dynode electron multiplier (AF562A, ETP).

Table 1. Instrument components and operating conditions

ICP generator
ICP-16
RF Plasma Products
Forward Power : 1100 W
Reflected Power : < 2 W
Frequency : 40.68 MHz
Plasma torch
Precision Glassblowing
Argon flow rates :
Plasma : 12 $Lmin^{-1}$
Auxiliary : 0.4 $Lmin^{-1}$
Carrier : 0.9 $Lmin^{-1}$
Interface
Sampler orifice (aluminum) : 1mm
Skimmer orifice (aluminum) : 0.7mm
Sampling depth : 10 mm
Vacuum
Interface : Rotary (SD450, Varian)
2nd : Diffusion (Crystal 202, Alcatel)
3rd : Turbo (ATS200, Alcatel)
Operating pressures
Interface : 1.5 torr
2nd : 5 x 10^{-4} torr
3rd : 1 x 10^{-6} torr
Mass Filter
Pole diameter : 16mm
200W, 150QC, Extrel
Prefilter
40mm long
Laboratory construction
Detector
AF 562A, ETP
Deflector : +230 V
Bias : - 2.6 kV

2.3 Chemical Tracer Method

Fig. 1 shows a schematic diagram of an experimental setup to test the chemical tracer method. If a liquid flows in the flow line of Fig. 1 at a flow rate of Q_0, and if a suitable chemical tracer (in this case 99.9% ^{7}Li) of known concentration C_{in} is injected through an injection point at a rate of Q_{in}, then mixture flow rate at

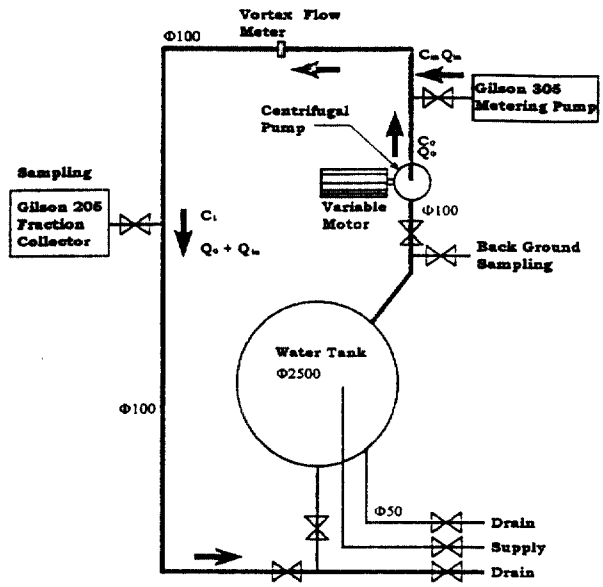

Fig. 1 Experimental setup for flow rate measurement by chemical tracer method

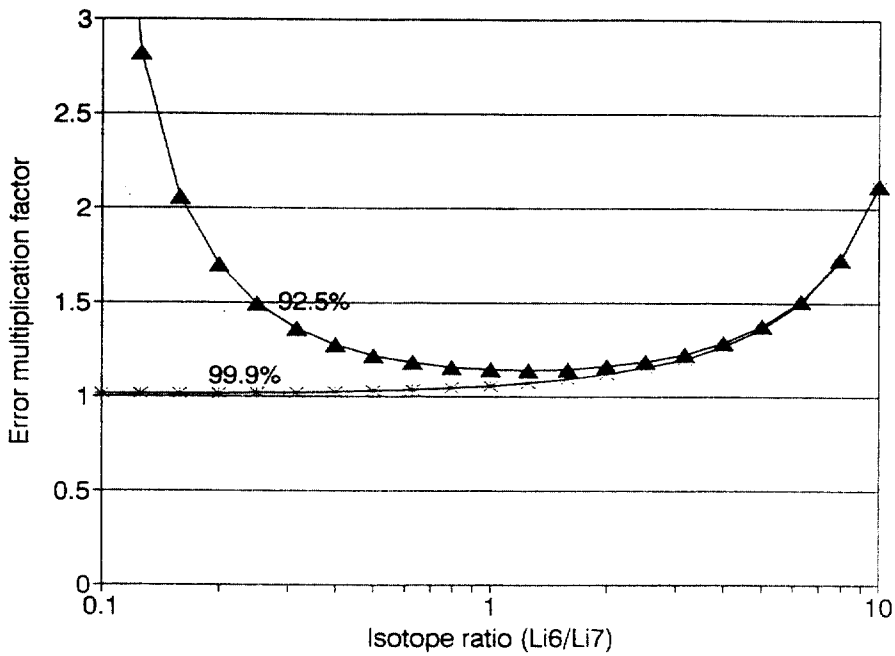

Fig. 2 Variation of error multiplication factor for two isotopic abundances of tracer (^{7}Li=92.5%, 99.9%) with 95% ^{6}Li spike

downstream of the injection point is given by $Q_o + Q_{in}$. When sufficient time has passed by, the law of conservation of mass requires that:

$$C_oQ_o + C_{in}Q_{in} = C_1(Q_o + Q_{in}) \quad (1)$$

After rearranging equation 1 for Q_o,

$$Q_o = \frac{C_{in} - C_1}{C_1 - C_o} \cdot Q_{in} \quad (2)$$

where C_1 is the tracer concentration of a sample withdrawn at downstream of the injection point and C_0 is background concentration of the tracer at upstream of the injection point. The tracer injection was accomplished with a calibrated metering pump (305, Gilson) with a dampener to reduce pulsation. Sampling was carried out with a fraction collector (FC205, Gilson).

3. Results and Discussion

3.1 Isotope Dilution Equation

Isotope dilution euqation can be derived by the following relationship between isotopes A and B :

$$R = \frac{A_s \cdot C_s \cdot W_s/M_s + A_{sp} \cdot C_{sp} \cdot W_{sp}/M_{sp}}{B_s \cdot C_s \cdot W_s/M_s + B_{sp} \cdot C_{sp} \cdot W_{sp}/M_{sp}} \quad (3)$$

where

R = isotope ratio (A/B) of spiked sample
A_s = atomic fraction of isotope A in sample
B_s = atomic fraction of isotope B in sample
A_{sp} = atomic fraction of isotope A in spike
B_{sp} = atomic fraction of isotope B in spike
C_s = analyte concentration in sample ($\mu g/g$)
C_{sp} = concentration of spike in solution ($\mu g/g$)
M_s = atomic weight of analyte in sample
M_{sp} = atomic weight of spike
W_s = weight of sample (g)
W_{sp} = weight of spike solution (g)

The final form of the equation is derived by solving equation 1 for Cs

$$C_s = \frac{C_{sp} \cdot W_{sp}}{Ws} \cdot \frac{M_s}{M_{sp}} \cdot \frac{A_{sp} - R \cdot B_{sp}}{R \cdot B_s - A_s} \quad (4)$$

C_{sp} is obtained by reverse isotope dilution with the primary standard. If equation 3 is solved for C_{sp}, equation 5 is derived

$$C_{sp} = \frac{Cp \cdot W_p}{W_{sp}} \cdot \frac{M_{sp}}{M_s} \cdot \frac{R^r \cdot B_s - A_s}{A_{sp} - R^r \cdot B_{sp}} \quad (5)$$

where

C_p = concentration of primary standard solution ($\mu g/g$)
W_p = Weight of primary standard solution in the spike calibration solution
W^r_{sp} = weight of spike solution in the spike calibraion solution
R^r = isotope ratio (A/B) of the spike calibration solution

Substituting equation 5 into equation 4, equation 6 is derived.

$$C_s = C_p \cdot \frac{W_{sp}}{W_s} \cdot \frac{W_p}{W^r_{sp}} \cdot \left(\frac{A_{sp} - R \cdot B_{sp}}{A_{sp} - R^r \cdot B_{sp}} \cdot \frac{R^r \cdot B_s - A_s}{R \cdot B_s - A_s} \right) \quad (6)$$

from equation 4, the following facts can be drawn :

1. As R approacher R^r, the term inside parenthesis gets close to 1 and consequently isotopic abundance errors of the sample and the spike become less significant.
2. If R is equal to R^r, analyte concentration in the sample is determined by the primary standard concentration times weight ratios of spike to sample
3. If the spike concentration is calibrated through the reverse isotope dilution, the term M_s/M_{sp} is cancelled out in equation 6 and hence it does not have to be included in equations 4 and 5.

Since a kilogram balance generally gives an uncertainty less than 0.001 %, concentration error of gravimetrically-prepared primary standard, and weight errors of spike and sample are negligible. Therefore, if spike concentration is calibrated through the reverse isotope dilution and if spike additions are carefully controlled to make the two isotope ratios R and R^r almost equal, then one obtains the

approximation equation for the standard deviation of the analyte concentration C_s by the law of propagation of errors.

$$s(Cs) \approx f(R) \cdot s(R) \quad (7)$$

where s = standard deviation

$f(R)$ = error multiplication factor for R

Thus precise measurement of R is essential for an accurate analytical result by the isotope dilution method.

From reference 5,

$$f(R) = \frac{(B_s/A_s - B_{sp}/A_{sp})/R}{(1/R - B_s/A_s)(B_{sp}/A_{sp} - 1/R)} \quad (8)$$

3.2 Optimization of Isotope Dilution

Using equation 8, the error multiplication factors were plotted in Fig. 2, for two isotopic abundances of the tracer (^{7}Li = 92.5% and 99.9%) with a spike isotope of 95% ^{6}Li. As can be seen clearly from Fig. 2, error multiplication factor of 99.9% ^{7}Li is close to 1 for the isotope ratios less than 1, though that of natural abundance Li becomes greater than 2 as the isotope ratios approach either 0.1 or 10. This is why the highly-enriched 99.9% ^{7}Li, instead of the natural abundance Li, was used as a chemical tracer injected into the feedwater line.

From an error multiplication point of view alone, the optimum isotope ratio is that which gives minimum error multiplication factor for given atomic fractions of sample and spike. Thus, differentiating equation 8 with respect to R and setting it equal to zero,

$$\text{Optimum ratio} = \left(\frac{A_s}{B_s}\frac{A_{sp}}{B_{sp}}\right)^{1/2} = 0.138 \quad (9)$$

In practice, however, isotope ratio measurement precision is more important and the best isotope ratio precision is achieved for ratios near one. Thus in this work, a compromised ratio of about 0.4 was chosen.

The final error of an analyte concentration caused by the spike enrichment uncertainty alone is defined by equation 10.

$$\text{Error} = \frac{C_s\ (\textit{false enrichment value})}{C_s\ (\textit{true enrichment value of } 0.95)} \quad (10)$$

The final error with spike concentration calibrated through the reverse isotope dilution can be estimated by substituting equation 6 into equation 10, and is plotted in Fig. 3 for isotope ratios (R) ranging from 0.1 to 1, with the isotope ratio of the spike calibration solution (R^r) fixed to 0.398. It can be seen from Fig. 3 that the error caused by 1 % error of the spike enrichment is negligible when spike additions are judiciously chosen so that difference between the two isotope ratios of spiked sample and spike calibration solutions is less than 20 %.

When the spike concentration is not calibrated through the reverse isotope dilution but fixed to a gravimetrically - calibrated value, the final error caused by false spike enrichment can be estimated by substituting equation 4 into equation 10. In Fig. 4 is plotted the estimated error for the isotope ratios of spiked sample ranging from 0.1 to 1. One can notice from Fig. 4 that the error keeps growing as the isotope ratio goes up, and that the error caused by 0.5 % error of the spike enrichment is greater than 0.5% even at practically minimum isotope ratio of 0.1.

3.3 Flow Rate Measurement by Chemical Tracer Method

20 samples were taken at 10 seconds interval 4 minutes after 50 ppm ^{7}Li injection and analyzed by the isotope dilution method. Flow rates were then calculated with the measured ^{7}Li concentration. In Fig. 5 is plotted the calculated flow rates by the chemical tracer method in comparison with those read by a vortex flow meter. Fig. 5 shows that the flow rates by the chemical tracer method are slightly higher than those by a vortex flow meter. This is because small contribution of ^{6}Li from background water at natural abundance lowers ^{7}Li concentration measured by the isotope dilution method, which raises the flow rates calculated by the chemical tracer method. If samples are collected too early then the injected sample is not fully mixed and the samples do not show steady but increasing ^{7}Li concentration. In Fig. 6 are plotted the calculated flow rates for 10 samples collected two minutes after sample injection. Fig. 6 clearly shows that the calculated flow rates keep going down due to insufficient mixing.

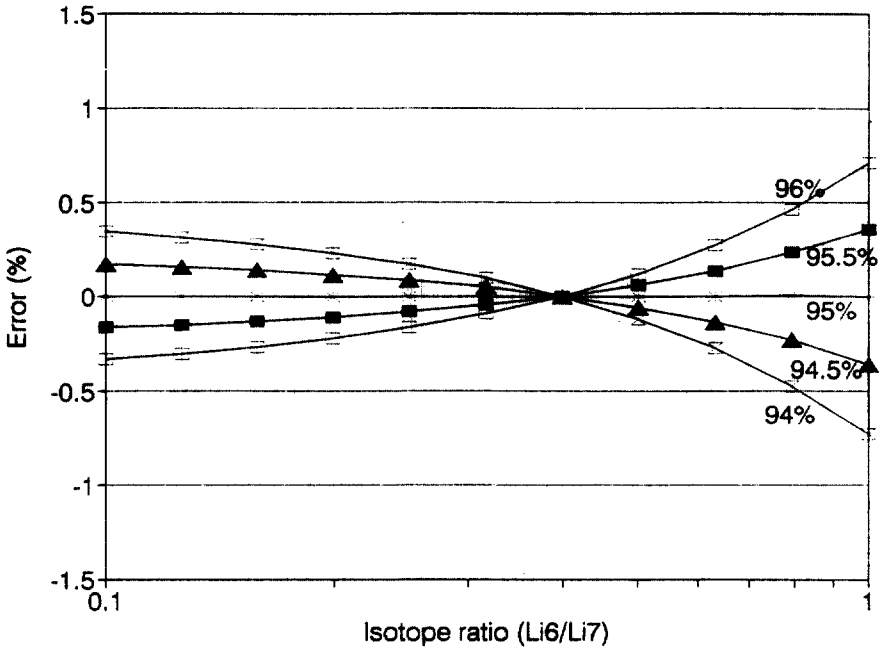

Fig. 3 Error variation due to false values of spike enrichment with spike concentration calibrated through reverse isotope dilution (isotope ratio of reverse isotope dilution = 0.4)

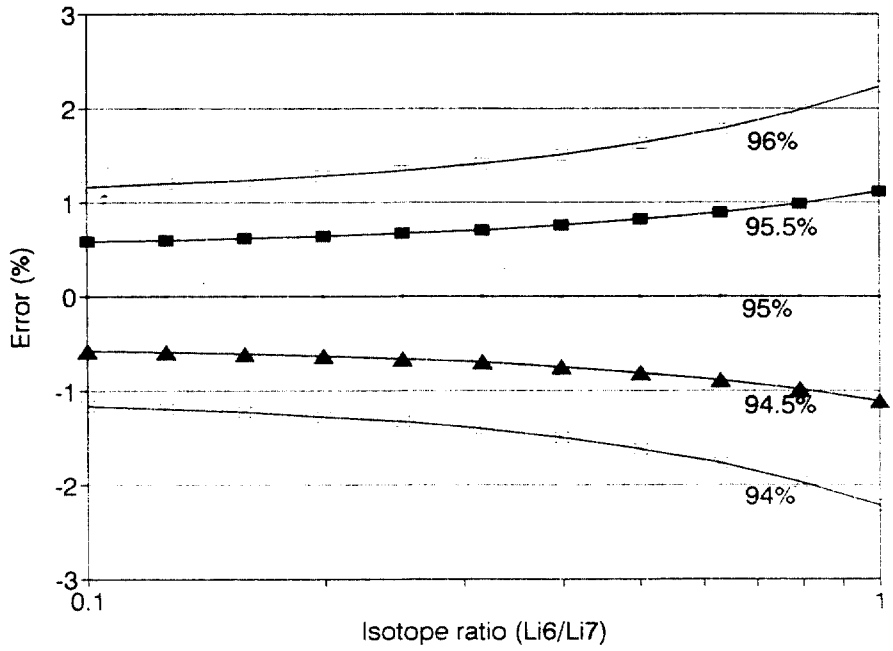

Fig. 4 Error variation due to false values of spike enrichment with a fixed spike concentration

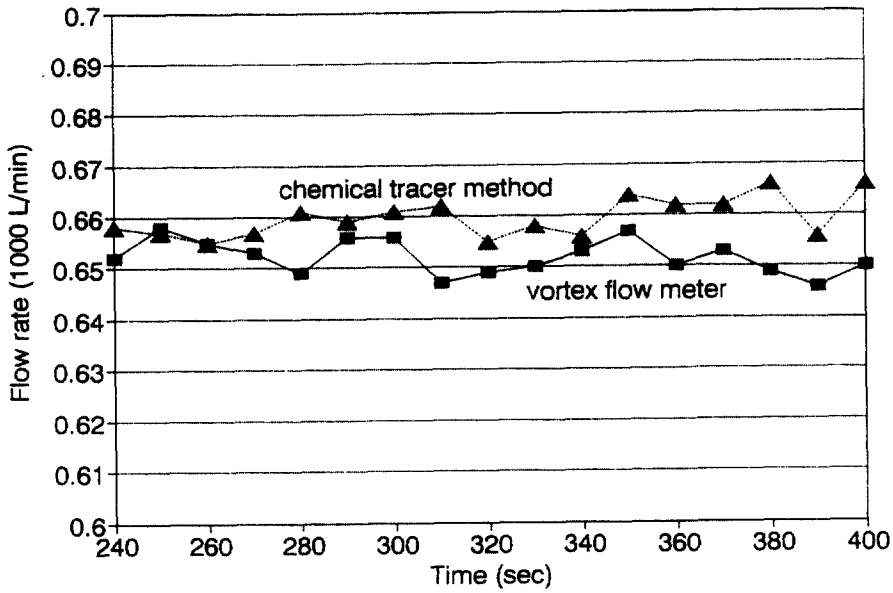

Fig. 5 Flow rate measurement by chemical tracer method (Samples collected 4 minutes after injection)

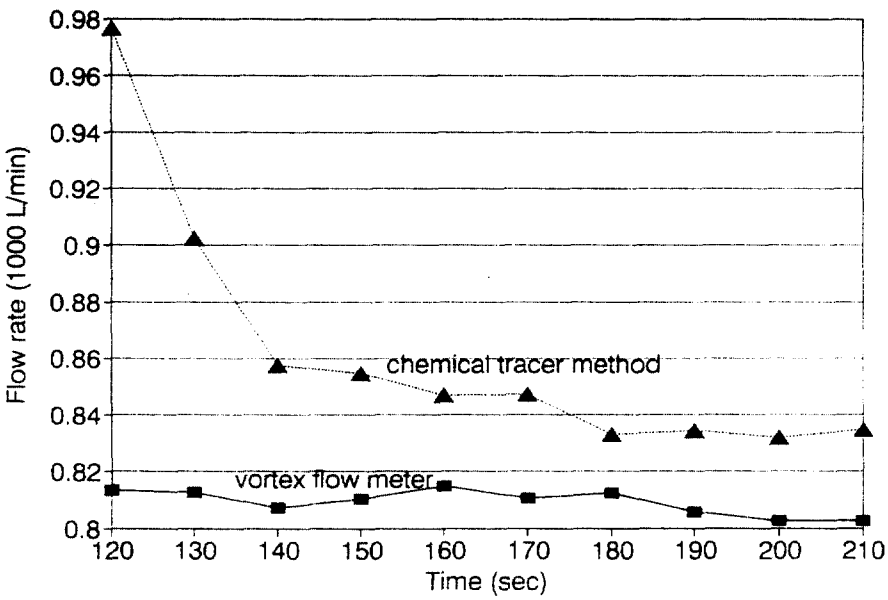

Fig. 6 Flow rate measurement by chemical tracer method (Samples collected 2 minutes after injection)

4. Conclusion

It has been found that spike calibration through the reverse isotope dilution can minimize potential error from uncertainties of isotopic abundances and that the samples should be collected after sufficient mixing to obtain steady flow rates. Compared with the flow rates read by a vortex flow meter, the chemical tracer method gives slightly higher values due to a small contribution of ^{6}Li from background. Therefore, it may be better to use an injection sample with natural abundance Li rather than 99.9 % ^{7}Li, when background Li is not negligible.

References

1. Sun, X. F., Ting, B. T. G., Zeisel, S. H., and Janghorbani, M., Analyst, 1987, 112, 1223.
2. Korean Semiconductor industry specification.
3. Development of Verification Methods for High Precision Flow Measurement - KRC 94Z S06, Report, 1995, 3-4.
4. Watters, R. L., the first draft on the isotope dilution mass spectrometry protocol for ICP-MS, April, 1995.
5. Riepe, W. and Kaiser, H., Fresenius Z. Anal. Chem., 1966, 223, 321.