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Determination of Lithium as a Chemical Tracer and Its Application to Flow Rate Measurements

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An isotope dilution equation is derived whereby the spike concentration is calibrated through so-called reverse isotope dilution with the primary standard solution. It is also demonstrated that potential systematic errors due to false spike enrichment values and the mass bias effect are minimized provided that spike additions are judiciously controlled so that the isotope ratio of the spiked primary standard solution does not differ from those of the spiked samples by more than 20%. Lithium was used as a chemical tracer to measure flow rates in an experimental test facility. Thirty-two samples were collected downstream of the injection point and analysed by isotope dilution ICP-MS. Six experiments were carried out on September 28 and November 8, 1995, to measure flow rates by the chemical tracer method. By optimizing the experimental conditions, the chemical tracer method gave flow rates that differed by $<0.4\%$ from the reference value.

Keywords: *Isotope dilution equation; reverse isotope dilution; inductively coupled plasma mass spectrometry; lithium; chemical tracer method; flow rate*

Introduction

Lithium is an important element determined in clinical laboratories because it is a therapeutic agent for manic-depressive illnesses.[1] In the earth sciences, lithium isotope ratios are measured to study rock formation. Lithium is also one of the important elements controlled in semiconductor process chemicals. For example, lithium should be controlled to below 1 ppb for the process chemicals used in 1 mega dynamic random access memories (DRAM).[2]

It is perhaps unfamiliar to most analytical chemists that lithium determinations can be used for an engineering application. In nuclear power plants, the 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 the pressure difference across a venturi. However, this measurement sometimes gives inaccurate flow rates owing to corrosion fouling, and a poorly developed velocity profile.[3] Thus, in order to measure the reactor thermal power correctly, the feedwater flow rate is measured independently using a chemical tracer method. As a chemical tracer, lithium is used because it is neither radioactive nor corrosive. Since injected lithium in the feedwater line should not affect the steam generator operation, its concentration in the feedwater line is generally limited to about 10 ppb. The lithium concentration of the feedwater sample must be determined with an uncertainty of $<0.2\%$, and at least 20 samples should be collected and analysed to delineate the variations from flow oscillation due to the control valve and disturbances. Such a high degree of accuracy and sample throughput can be achieved by the isotope dilution method combined with ICP-MS. This combination has been applied in the various analytical fields such as the certification of reference materials,[4,5] medicine,[6] geology,[7] and quality control.[8]

The CIPM (Comité International des Poids et Mésures) has established a Working Group on Metrology in Chemistry, which has undertaken an interlaboratory comparison programme with the isotope dilution method as a reference method. However, the accuracy and precision of the isotope dilution data reported by most laboratories were not satisfactory, probably owing to the inexperience of the participating laboratories with the technique.[9] In order to clarify areas of uncertainty in dealing with the isotope dilution technique, the National Institute of Standards and Technology (NIST) proposed an experimental protocol[10] for the isotope dilution method and emphasized the importance of spike calibration through so-called 'reverse isotope dilution' with the primary standard to minimize potential systematic errors.

In this work, lithium, as a chemical tracer, was measured by following the isotope dilution protocol and the feasibility of the chemical tracer method for the measurement of flow rates was investigated.

Experimental

Enriched Isotopes and Reagents

Enriched ^{6}Li (95.5%) metal was obtained from US Services (Summit, NJ, USA) and Li foil (natural abundance) was purchased from Cyprus Foote Mineral (Exton, PA, 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. Lithium isotopic reference material in carbonate (LSVEC, RM8545) was bought from NIST (Gaithersburg, MD, USA). After drying at 140 °C for 1 h, 0.5324 g of the isotopic reference material was dissolved in 200 ml of de-ionized water to make a 500 ppm stock standard solution. All the prepared solutions were acidified to 1% m/m nitric acid with ultra-pure nitric acid (Dong Woo Chemical, Iksan, Chunbuk, Korea).

Instrumentation

The ICP-MS instrument employed in this work was a laboratory-constructed unit. Fig. 1 depicts the mass spectrometer part. Instrument components and operating conditions are given in Table 1. For sample introduction, a Meinhard concentric nebulizer (TR-30-C1) and a Scott-type spray chamber were used with a peristaltic pump (Minipuls 3; Gilson, Villiers-le-Bel, France) to control the sample uptake rate. An off-axis ion lens was used in this instrument where its quadrupole and interface centres were 8 mm apart. Ions exiting the quadrupole filter were deflected 90° into the mouth of a discrete dynode electron multiplier (AF562A, ETP Scientific, Auburn, MA, USA). Li isotope ratios were measured in the scan mode with 16 channels per unit mass. The dwell time was set to 2 ms per channel and the counts on each channel were accumulated for 0.6 s (300 sweeps). The accumulated data were transferred to a personal computer through GPIB (general-purpose interface bus) and isotope ratios were calculated by integrating ±0.2 u intervals.

Chemical Tracer Method

In Fig. 2, water in the tank flows through the tube of 203.2 mm diameter. At the background sampling point, samples are taken to determine background concentration (C_0) of the tracer in the water tank. At the injection point, a chemical tracer (in this case Li) of known concentration C_{in} is injected at a rate Q_{in} by a calibrated metering pump (model 305; Gilson) with a damper to reduce pulsation. A reference flow meter is installed downstream of the injection point to obtain a reference flow rate. When sufficient time has passed, water samples of tracer concentration C_1 are collected at the sampling point with a fraction collector (FC205; Gilson). The flow rate Q_0 can be determined by applying the law of conservation of mass in the flow system in Fig. 2:

$$C_0Q_0 + C_{in}Q_{in} = C_1(Q_0 + Q_{in}) \qquad (1)$$

After rearranging:

$$Q_0 = \frac{C_{in} - C_1}{C_1 - C_0} \times Q_{in} \qquad (2)$$

A chemical tracer should satisfy the following conditions: easily diluted with water; not corrosive; not radioactive; and not toxic. Of the possible candidate elements that satisfy the above conditions, Li was chosen as a tracer in this experiment. For a reference flow meter, a turbine meter (HTF300; Hitrol, Pajoo, Kyungki, Korea) that had traceability to the flow rate standard of Korea Research Institute of Standards and Science (KRISS) was employed.

Preparation of Solutions

An electronic balance (HX-400; A&D, Tokyo, Japan) was used for the preparation of solutions. This balance has a weighing capacity of 410 g and a repeatability of 0.001 g.

1. Injection solution. The water tank depicted in Fig. 2 can hold about 50 tons of water and was filled with underground water owing to shortage of tap water. As the Li concentration of the underground water was found to be not negligible (about 2.5 ppb), the isotopic composition of the injection solution (C_{in}) should be the same as that of the underground water so that Li measurements by the isotope dilution method can be consistent for both background solutions (C_0) and solutions taken at sampling point (C_1). A 200 ppm injection solution was prepared by dissolving the Li foil of natural abundance in de-ionized water.

2. Spike solution. An appropriate amount of ^{6}Li metal was dissolved in de-ionized water to make a ^{6}Li stock standard solution. An approximately 0.5 ppm spike solution was prepared by diluting this stock standard solution. An accurate concentration of this solution is not required and is to be determined by the reverse isotope dilution.

3. Primary standard solution. Solution 1 was diluted to about 1 ppm and the diluted solution was used as a primary standard solution for the reverse isotope dilution. The absolute concentration of the injection solution is not important but the dilution ratio is actually counted. This is because, in eqn. (2), any bias factor of C_{in} is cancelled out if C_0 and C_1 are measured with reference to C_{in}.

4. Spiked sample solution. About 50 ml of water were collected at the downstream sampling point and an appropriate amount of solution 2 was added to the sample solution so that its isotope ratio was close to 1.

5. Spiked background sample solution. About 100 ml of water were collected at the background sampling point and an appropriate amount of solution 2 was added to the background solution so that its isotope ratio was close to 1.

6. Spike calibration solution. A 1 g amount of solution 3 was mixed with 2 g of solution 2 and then the mixture was diluted to

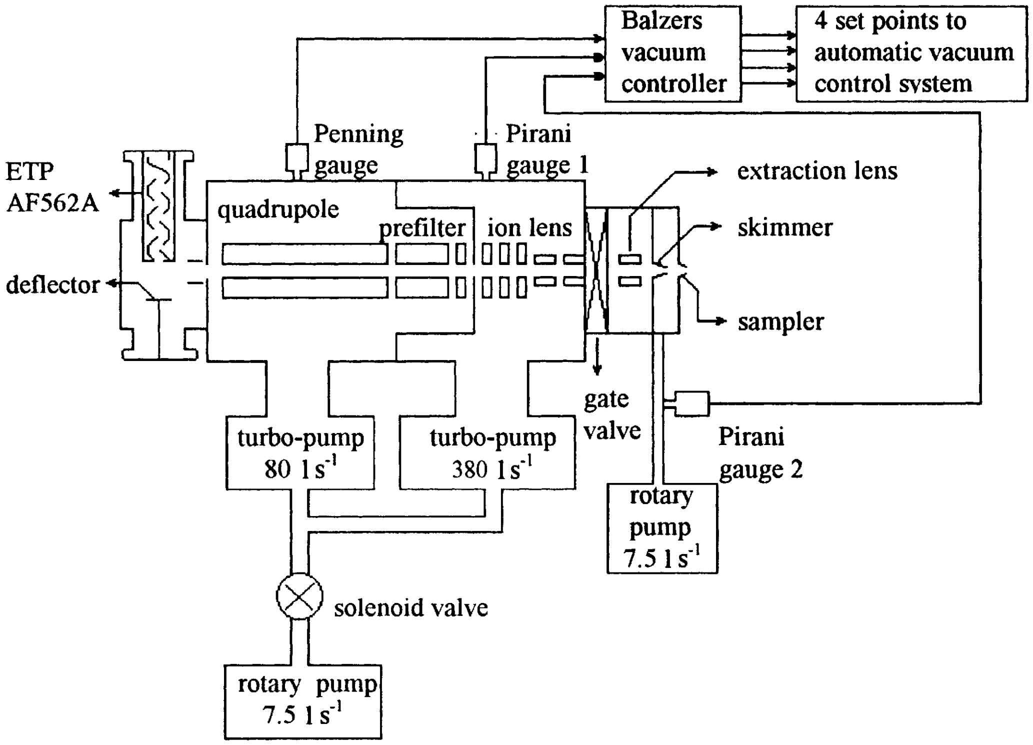

Fig. 1 Schematic diagram of ICP-MS system.

about 100 g. Isotope ratios of this solution were measured after every three spiked samples to correct for the mass bias drift.

7. Isotopic reference solution. A 500 ppm isotopic reference solution (NIST RM8545) was serially diluted to about 10 ppb and the isotope ratio of this solution was measured to obtain a mass bias correction factor. In the course of the isotope dilution calculation, all the measured isotope ratios of solutions 4, 5 and 6 were multiplied by the correction factor.

Table 1 Instrument components and operating conditions

Component	Operating conditions
ICP generator—	
ICP-16 (RF Plasma Products)	Forward power: 1100 W Reflected power: < 2 W Frequency: 40.68 MHz
Plasma torch—	Argon flow rates—
Precision glassblowing	Plasma: 12 l min^{-1} Auxiliary: 0.4 l min^{-1} Carrier: 0.9 l min^{-1} Sample uptake rate: 0.7 ml min^{-1}
Interface	
Sampler orifice (aluminium): 1 mm	Sampling depth: 10 mm
Skimmer orifice (aluminium): 0.7 mm	
Vacuum—	Operating pressures—
Interface: rotary (2020A, Alcatel)	Interface: 1.5 Torr
2nd: turbo (5402CP, Alcatel)	2nd: 5 × 10^{-4} Torr
3rd: turbo (5080CP, Alcatel)	3rd: 1 × 10^{-6} Torr
Mass filter—	
16 mm pole, 220 mm long	
200 W, 150QC, Extrel	
Pre-filter—	
16 mm pole, 40 mm long	
Laboratory construction	
Detector—	
AF 562A, ETP	Deflector: +230 V Bias: −2.6 kV

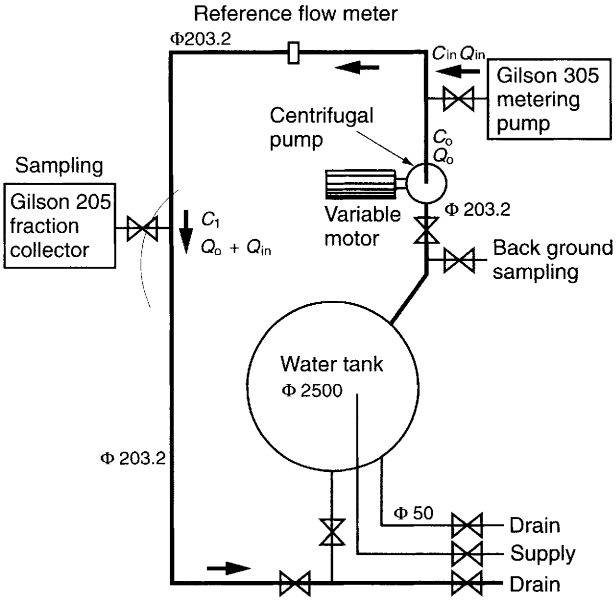

Fig. 2 Experimental facilities for flow rate measurement by chemical tracer method.

Results and Discussion

Isotope Dilution Equation

The molar ratio of isotope A to isotope B in a spiked sample can be expressed by

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

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 (μg g^{-1}); C_{sp} = concentration of spike in solution (μg g^{-1}); M_s = atomic mass of analyte in sample; M_{sp} = atomic mass of spike; W_s = mass of sample (g); and W_{sp} = mass of spike solution (g).

The isotope dilution equation for C_s is derived by rearranging eqn. (3):

$$C_s = \frac{C_{sp} W_{sp}}{W_s} \times \frac{M_s}{M_{sp}} \times \frac{A_{sp} - R B_{sp}}{R B_s - A_s} \tag{4}$$

C_{sp} is obtained by reverse isotope dilution with the primary standard. If eqn. 3 is rearranged for C_{sp}, we obtain

$$C_{sp} = \frac{C_p W_p}{W^r_{sp}} \times \frac{M_{sp}}{M_{st}} \times \frac{R^r B_s - A_s}{A_{sp} - R^r B_{sp}} \tag{5}$$

where C_p = concentration of primary standard solution (μg g^{-1}); W_p = mass of primary standard solution in spike calibration solution; W^r_{sp} = mass of spike solution in spike calibration solution; R^r = isotope ratio (A/B) of spike calibration solution; and M_{st} = atomic mass of analyte in primary standard solution.

In this work, the difference between the two atomic masses M_s and M_{st} is negligible, because the same injection solution is used as a primary standard solution. Substituting eqn. (5) into eqn. (4), the final form of isotope dilution equation is obtained:

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

From eqn. (6), the following facts can be deduced: as R approaches R^r, the term inside parentheses becomes close to 1 and consequently isotopic abundance errors of the sample and the spike become less significant; and if the spike concentration is calibrated through the reverse isotope dilution, the term M_s/M_{sp} is cancelled out in eqn. (6).

Since the electronic balance used in this work gives an uncertainty of 0.05–0.001% depending on solution masses, the concentration error of the gravimetrically prepared primary standard and the mass errors of the spike and sample are negligible. Therefore, if the 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 from the law of propagation of errors:[11]

$$s(C_s) \approx f(R) s(R) \tag{7}$$

where s = standard deviation and $f(R)$ = error multiplication factor for R. Hence the precise measurement of the isotope ratio R is essential to obtain an accurate analytical result by the isotope dilution method.

Determination of Systematic Errors

Depending on its origins, the isotopic composition of an element may be slightly different.[12] For an enriched isotope, its isotopic composition is generally provided by the vendor, and an accurate measurement of its isotopic composition is difficult because of very large differences in abundances. Further, its isotopic composition could be slightly altered owing to the contamination during preparation at a suitable concentration for spiking. The isotope ratios of spiked sample solutions and spike calibration solutions measured by ICP-MS are generally different from the true ratios because of the mass bias effect. The true ratio of Li, $({}^6\text{Li}/{}^7\text{Li})_t$, can be related to the measurement ratio, $({}^6\text{Li}/{}^7\text{Li})_m$, by the equation

$$({}^6\text{Li}/{}^7\text{Li})_m = ({}^6\text{Li}/{}^7\text{Li})_t(1+a) \qquad (8)$$

where a is the bias per mass unit[13] and the mass bias effect can be corrected with isotopic reference materials with certified ratios. However, the mass bias correction drifts throughout a working day, especially at low mass as with Li. Hence potential systematic errors from uncertainties in isotopic compositions and the mass bias effect were estimated for Li measurements in this work. The error of an analyte concentration caused by a false spike enrichment value or a false isotope ratio due to the mass bias drift can be calculated with eqns. (6) and (9) when the spike concentration is calibrated through the reverse isotope dilution:

$$\text{Error }(\%) = 100\left[\frac{C_s(\text{false value})}{C_s(\text{true value})} - 1\right] \qquad (9)$$

The calculated errors are plotted in Fig. 3(*a*) and (*b*) for isotope ratios (R) ranging from 0.2 to 5, with the isotope ratio of the spike calibration solution (R^r) fixed at 1. It can be seen that the error caused by a 0.5% error in the spike enrichment or mass bias of 0.02 is negligible when spike additions are judiciously controlled so that the isotope ratio of the spike calibration solution does not differ from those of the spiked samples by more than 20%.

When the spike concentration is not calibrated through the reverse isotope dilution but fixed at a gravimetrically calibrated value, the final error caused by the false spike enrichment or mass bias effect can be calculated with eqns. (4) and (9). In Fig. 3(*c*) is plotted the estimated error from four false enrichment values when the isotope ratios of spiked sample

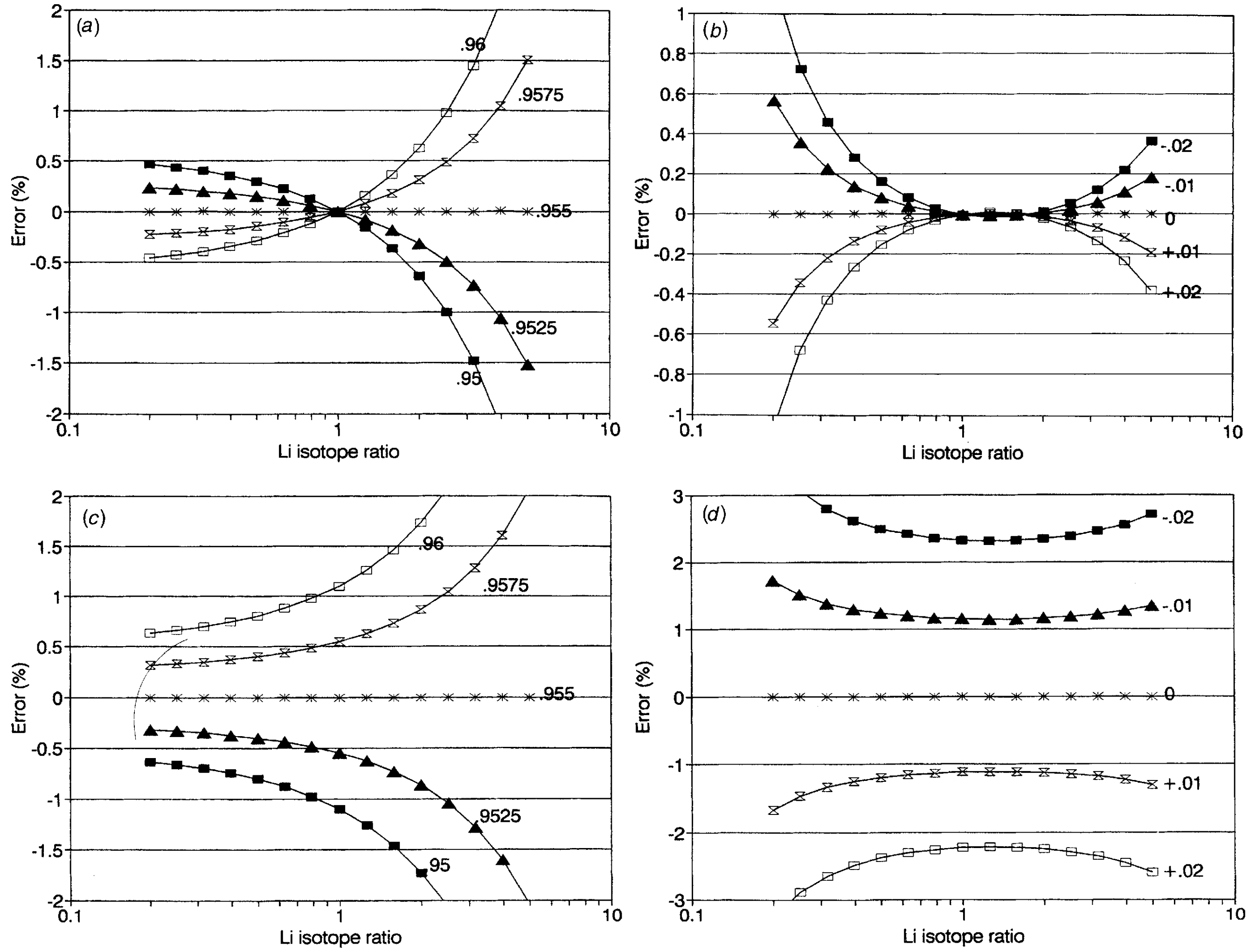

Fig. 3 (*a*) Calculated error from false enrichment value *versus* isotope ratio of spiked sample when the spike concentration is calibrated through reverse isotope dilution and the isotope ratio of spike calibration solution (R^r) is fixed at 1. (*b*) Calculated error from mass bias *versus* isotope ratio of spiked sample when spike concentration is calibrated through reverse isotope dilution and the isotope ratio of spike calibration solution is fixed at 1. (*c*) Calculated error from false enrichment value *versus* isotope ratio of spiked sample when a fixed spike calibration is used without going through reverse isotope dilution. (*d*) Calculated error from mass bias *versus* isotope ratio of spiked sample when a fixed spike concentration is used without going through reverse isotope dilution.

varies between 0.2 and 5. It can be seen that the error continues to grow as the isotope ratio increases, and that the error caused by a 0.5% error of the spike enrichment is >0.5% even at the practically minimum isotope ratio of 0.2. In Fig. 3(*d*) is plotted the estimated error from four mass bias values. Fig. 3(*d*) shows that error from such a small mass bias of 0.01 is calculated to be always >1% and that the error does not change rapidly as the isotope ratio of the spiked sample changes.

Table 2 Determination of Li concentrations for six experiments carried out on September 28 and November 8, 1995

	Li concentration (ppb)					
	Sept. 28			Nov. 8		
Sample No.	A	B	C	A	B	C
1	12.474	11.489	11.981	12.226	12.495	12.347
2	12.371	11.281	11.973	12.358	12.358	12.378
3	12.407	11.047	11.794	12.383	12.503	12.420
4	12.245	11.032	11.797	12.365	12.474	12.496
5	12.303	11.085	11.935	12.444	12.487	12.434
6	12.749	11.042	11.794	12.299	12.415	12.327
7	12.700	11.162	11.917	12.388	12.387	12.333
8	12.733	11.187	11.899	12.496	12.310	12.403
9	12.623	11.060	11.863	12.353	12.260	12.293
10	12.690	11.290	11.945	12.333	12.237	12.513
11	12.650	11.106	11.885	12.293	12.354	12.268
12	12.400	11.199	11.757	12.257	12.356	12.307
13	12.437	11.143	11.901	12.441	12.419	12.241
14	12.401	11.210	11.907	12.253	12.453	12.373
15	12.340	11.247	11.915	12.281	12.430	12.231
16	12.395	11.176	11.842	12.360	12.377	12.272
17	12.374	11.353	11.937	12.308	12.296	12.308
18	12.315	11.289	11.911	12.436	12.383	12.367
19	12.358	11.410	12.065	12.324	12.249	12.503
20	12.343	11.262	12.035	12.255	12.410	12.320
21	12.489	11.202	11.972	12.365	12.222	12.305
22	12.316	11.128	11.948	12.232	12.282	12.397
23	12.642	11.247	11.979	12.404	12.328	12.256
24	12.582	11.136	11.968	12.493	12.447	12.326
25	12.573	11.124	11.895	12.243	12.506	12.248
26	12.308	11.105	12.033	12.275	12.484	12.457
27	12.379	11.182	12.006	12.495	12.375	12.488
28	12.350	11.168	12.012	12.362	12.352	12.427
29	12.452	11.166	11.897	12.365	12.388	12.338
30	12.472	11.174	12.040		12.366	12.295
31					12.324	12.345
Mean	12.462	11.190	11.926	12.347	12.378	12.355
$\pm 1\ s$	±0.145	±0.106	±0.078	±0.080	±0.081	±0.081
RSD (%)	1.17	0.95	0.66	0.65	0.65	0.65

Flow Rate Results

Six experiments were carried out on September 28 and November 8, 1995, to measure flow rates by the chemical tracer method. In each experiment 32 samples were collected at 5 s intervals after the injection of 150 or 200 ppm Li solution and spiked with ^{6}Li spike solution immediately after collection. For each set of 32 samples analysed by the isotope dilution method, some data that were far from the average value were rejected. Between samples, 5% m/m HNO_3 cleaning solution was aspirated for 1 min and then the ^{7}Li signal was observed to decay from about 100 000 to below 200 counts. No significant memory effects were observed.

Table 2 shows six sets of Li concentrations and the precision. The relatively poor precision of Li determinations is attributed to the mass bias drift at this low mass caused by about 80 ppm matrix elements (60 ppm Ca, 12 ppm Na, 9 ppm Mg and 1 ppm K) present in the underground water used in this experiment. For a spike calibration solution without a matrix the precision of Li isotope ratio measurements was about 0.2% RSD, whereas for each spiked sample the precision was generally between 0.5 and 0.8% RSD. The mass bias of this system calculated with eqn. (8) was about −0.13 and it generally shifted in one direction by about 0.5–1% after three sample measurements (about 18 min). In order to correct the mass bias drift, the isotope ratio of the spike calibration solution was measured after every three spiked samples and an interpolated ratio was applied to each spiked sample. Table 2 also shows that the precision of Li determination for the September 28 samples is even poorer than that for the November 8 samples. This is probably because for the experiments carried out on September 28 the samples were collected 60 s after solution injection, whereas for those on November 8 they were collected 90 s after solution injection.

In Table 3 are given two sets of measured background concentrations. As the water tank was refilled at the start of each

Table 3 Determination of background Li concentrations

	Li concentration (ppb)	
No.	Sept. 28	Nov. 8
1	2.658	2.521
2	2.676	2.528
3	2.656	2.509
4	2.675	2.501
5	2.653	2.520
Mean ± 1 *s*	2.663 ± 0.011	2.515 ± 0.010
RSD (%)	0.41	0.42

Table 4 Mean flow rates and experimental parameters

	Test date (1995)					
	Sept. 28			Nov. 8		
Parameter	A	B	C	A	B	C
Concentration of injection solution (ppm)	150	150	200	200	150	200
Injection rate/ml min^{-1}	99.053	99.055	99.053	98.927	98.927	98.927
No. of samples	30	30	30	29	31	31
Flow rate by chemical tracer method (mean ± 1 *s*)/ 10^3 l min^{-1}	1.5183 ±0.0224	1.7411 ±0.0215	2.1401 ±0.0182	2.0122 ±0.0163	1.5044 ±0.0122	2.0106 ±0.0165
Flow rate by reference flow meter (mean ± 1 *s*)/ 10^3 l min^{-1}	1.4954	1.6990	2.1475	2.0186 ±0.0027	1.4997 ±0.0018	2.0029 ±0.0023
Difference (%)	+1.53	+2.47	−0.34	−0.31	+0.31	+0.38

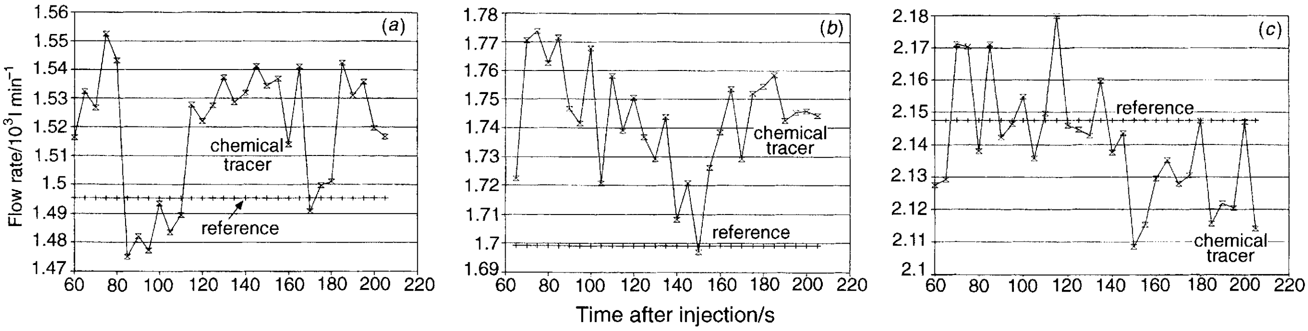

Fig. 4 Flow rates by the chemical tracer method *versus* time after injection for three sets of experiments carried out on September 28, 1995: (*a*) experiment A; (*b*) experiment B; and (*c*) experiment C.

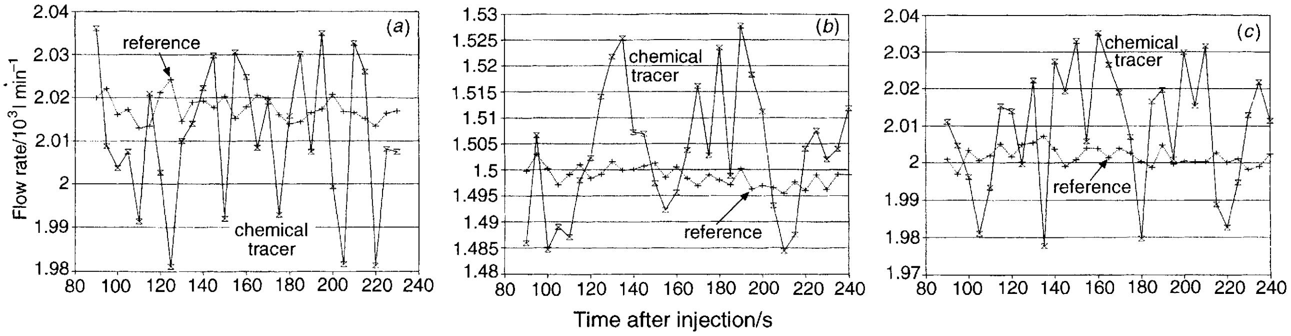

Fig. 5 Flow rates by the chemical tracer method *versus* time after injection for three sets of experiments carried out on November 8, 1995: (*a*) experiment A; (*b*) experiment B; and (*c*) experiment C.

day's experiments, one day's background value is slightly different from another's. In Table 4 are given the mean flow rates obtained by the chemical tracer method and reference meter together with the experimental parameters such as concentration of injection solution (C_{in}) and injection rate (Q_{in}). Tables 2 and 4 indicate that the poorer precision of Li determinations is closely related to the larger error of the flow rates in the chemical tracer method, and that the chemical tracer method gives flow rate measurements with less than a 0.4% difference from the reference flow rate except for two experiments on September 28. In Figs. 4 and 5 are plotted six sets of measured flow rates *versus* sampling time in comparison with the reference flow rates for the experiments carried out on September 28 and November 8, respectively.

Conclusion

It has been demonstrated that errors from minor uncertainties of isotopic compositions or the small mass bias effect can be minimized if the spike concentration is calibrated through reverse isotope dilution, and if the spike calibration solution is prepared such that its isotope ratio does not differ from those of the spiked samples by more than 20%.

The precision of Li determinations was not satisfactory because of the matrix elements present in the underground water, yet the flow rates measured by the chemical tracer method agreed well with those obtained by the reference meter. As the feedwater of nuclear power plants has a negligible matrix content, the chemical tracer method would give more precise and accurate flow rate measurements if applied to nuclear power plants.

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