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Isotope ratio measurements of magnesium and determination of magnesium concentration by reverse isotope dilution technique on small amounts of ^{26}Mg-spiked nutrient solutions with inductively coupled plasma mass spectrometry

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Abstract

In the present work, an analytical method has been developed for the measurement of magnesium isotope ratios and the determination of magnesium concentration in ^{26}Mg-spiked plant nutrient solutions by the reverse isotope dilution technique. The experimental parameters of the mass spectrometric measurements using quadrupole-based inductively coupled plasma mass spectrometry (ICP-MS) were optimized with respect to the lowest relative standard deviation (RSD) in the magnesium isotopic ratio (^{25}Mg/^{24}Mg and ^{26}Mg/^{24}Mg). The RSD of the measured isotopic ratios was determined in different concentrations of isotopic standard solution (NIST SRM 980T^{26}Mg-enriched isotopic standard) of natural isotopic abundances (from 1 to 50 μg/L with 1.9% to 0.22% RSD, respectively). Long-term isotopic ratio measurements using 50 μg/L isotopic standard solution (NIST SRM 980) yielded 0.14% RSD for ^{25}Mg/^{24}Mg and 0.23% RSD for ^{26}Mg/^{24}Mg. The accuracy of measured isotopic ratios was 0.1% to 0.3% [^{25}Mg/^{24}Mg 0.12684 ± 0.00018 (measured) versus 0.12663 ± 0.00013 (certified) and ^{26}Mg/^{24}Mg 0.13958 ± 0.00036 (measured) versus 0.13932 ± 0.00026 (certified)]. Synthetic isotopic mixtures of NIST SRM 980 and highly enriched ^{26}Mg solutions were prepared and the measured isotopic ratios were compared with the calculated ones. The RSD of the isotope ratios measurements ranged between 0.14% to 0.07% for the ^{25}Mg/^{24}Mg ratio and 0.2-0.04% for the ^{26}Mg/^{24}Mg ratio. The developed method has been successfully applied for the determination of the magnesium isotope ratios and the concentration measurements in ^{26}Mg-enriched plant nutrient solution samples with reverse isotope dilution technique. The nutrient solutions investigated contained high amounts of calcium and potassium (20–35 μg/ml and 9.7–30 μg/ml, respectively). Magnesium concentrations were determined by inductively coupled plasma optical emission spectrometry (ICP-OES) and ICP-MS with external calibration and the measured values are in agreement with the results obtained by the reverse isotope dilution technique. (Int J Mass Spectrom 202 (2000) 231–240) © 2000 Elsevier Science B.V.

Keywords: Magnesium, inductively coupled plasma mass spectrometry, isotope ratio measurements, trace analysis.

1. Introduction

Inductively coupled plasma mass spectrometry (ICP-MS) is widely used in different fields of science and technology, especially in the trace and ultratrace

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analysis of environmental, biological and geological samples, high-purity materials, natural and waste waters and industrial products [1–3]. The capability of ICP-MS for precise isotope ratio measurement has increasing importance for the determination of stable isotopes and long-lived radionuclides [4,5], for example, for determination of geological age (geochronology) and isotope variations in environmental, geological and cosmic samples and in radioactive waste materials [6–15]. Using enriched stable isotopes tracer experiments have been reported studying the bioavailability, metabolism [16], and toxicity of the analyte of interest for biological and medical research [17–22]. Furthermore, isotope ratio measurements are especially important in trace element determination and element speciation by isotope dilution mass spectrometry (IDMS), which provides precise and accurate analytical results [23,24].

In the past, for isotope ratio measurements of elements with an ionization potential <8 eV thermal ionization mass spectrometry (TIMS) has been used most frequently because of its excellent precision (down to 0.002% using multi-ion collection instruments) and accuracy [17]. For these measurements the analyte of interest is separated from the matrix, for example, using extraction, precipitation, or ion-exchange methods, which makes sample preparation difficult and time consuming. In the past few years inductively coupled plasma mass spectrometry has become more important for precise isotope ratio and isotope dilution measurements. ICP-MS has severa; advantages over TIMS, including excellent sensitivity, precision and ease of sample preparation [12]. Limiting factors for ICP-MS are interference from molecular ions and atomic ions of the analytes, the dead time of the detector used, stability of the ion current and space charge effects in the interface and ion optics region [4].

Among inductively coupled plasma mass spectrometers, quadrupole-based instruments (ICP-QMS) are the most commonly used. The precision of short-term isotopic ratio measurement is 0.1% to 0.5% with these instruments, while a precision of 0.028% is possible in long-term measurements [12]. Double focusing sector field ICP mass spectrometers were used to achieve the increased sensitivity and precision. Typical relative standard deviations for short-term measurements of isotope ratios range between 0.2% and 0.05%. An improved precision in short-term stability of 0.026% was observed by double-focusing sector field ICP-MS with a shielded torch [6]. Further impovement in the precision down to 0.002% is possible using sector field ICP mass spectrometers equipped with a multiple ion collector system [17].

An interesting research topic at the Research Centre Jülich is the investigation on the distribution and transport of mineral elements in plants. For example, magnesium has great importance as an essential element in the biochemical processes of plants. However, magnesium deficiency is a widespread phenomenon in central European forests because of soil acidification observed mainly in industrial areas [25]. In a recent paper, magnesium isotopic ratio measurements were performed in plant tissue samples with double-focusing sector field ICP-MS and the laser ionization mass spectrometry using a LAMMA 500 (Leybold Heraeus, Cologne, Germany) and the lateral distribution of magnesium isotopes in some solid plant tissues were studied with secondary ion mass spectrometry (SIMS) [7]. Such tracer experiments serve for investigations on the distribution and transport of magnesium in plants to explain the mechanism of magnesium uptake and distribution [26]. Of interest is that the ^{26}Mg/^{24}Mg isotope ratio, measured with the LAMMA at low mass resolution, was higher due to the interference of $^{12}C^{14}N^+$ on $^{26}Mg+$ than the ICP-MS results (at mass resolution of $m/\Delta m = 3000$). The reported relative standard deviations (RSD) of ^{26}Mg/^{24}Mg and ^{25}Mg/^{24}Mg isotope ratios in aqueous isotopic standard solutions were about 0.5% with double-focusing ICP-MS ($m/\Delta m = 3000$, 50 μg/L) and approximately 3% with LAMMA ($m/\Delta m = 500$), respectively [7].

In the present work we performed magnesium isotope ratio and reverse isotope dilution measurements for tracer experiments in biological research on ^{26}Mg–spiked plant nutrient solutions. The results of determination of Mg concentration were compared to the values measured by ICP-MS and ICP-OES using

Table 1
Instrumental parameters and measurement conditions using the ICP-QMS Elan 6000 (Perkin-Elmer, Sciex)

ICP-MS	
Radiofrequency power	1375 W
Coolant Ar flow rate	17 L/min
Auxiliary Ar flow rate	1.2 L/min
Nebulizer Ar flow rate	0.87 L/min
Sample uptake rate	0.085 mL/min
sample size	6.52 ng
Nebulizer type	Micronmist (microconcentric micronebulizer)
Spray chamber	Minicyclonic, Cinnabar
Sampler cone	Nickel, 1.1 mm orifice diameter
Skimmer cone	Nickel, 0.9 mm orifice diameter
Dwell time	10 ms
Integration time	2000 ms
Detector dead time	65 ns
Sweeps/reading	200
Readings/replicate	1
Replicates	10

external calibration. To reduce the required sample amount, micronebulization was applied for sample introduction allowing the analysis of very small liquid samples taken from different locations of the plant to determine tissue-specific isotope distributions.

2. Experimental

2.1. Instrumental

For the measurement of magnesium isotope ratios, the Elan-6000 quadrupole-based ICP-MS (Perkin-Elmer Sciex, Concord, Ontario, Canada) was used. A microconcentric nebulizer (Micromist AR30-1-FN02, Glass Expansion, Australia) and the Cinnabar Minicyclonic spray chamber (Glass Expansion, Australia) were applied for sample introduction to minimize the sample uptake rate [4]. ICP-OES measurements were carried out with the Thermo Jarrel Ash IRIS Duo instrument. Instrumental parameters and operating conditions are summarized in Table 1.

2.2. Chemicals

For method development and isotope dilution, the NIST SRM 980 isotopic standard with natural isotopic composition [27] and dissolved ^{26}Mg-enriched MgO of Russian origin (isotope composition: ^{24}Mg 1.82%, ^{25}Mg 1.08% and ^{26}Mg 97.1%) were used. Solutions were prepared and diluted with high-purity deionized water obtained from a Milli-Q-Plus water purification system. The acid content of the samples was set to 2% with suprapure nitric acid (Merck, Darmstadt, Germany) which was further purified by subboiling-point distillation.

2.3. Samples and sample preparation

Isotopic laboratory standard solutions of ~100 μg/ml concentration were prepared from the solid standard material (Mg metal in the case of NIST SRM 980 and ^{26}Mg-enriched MgO powder) by dissolving a known amount of the solid in dilute nitric acid. The concentration of the stock solutions obtained was validated by ICP-OES. For instrument optimization 10μg/L NIST SRM 980 solution was used. 50 μg/L solution of the same isotope standard solution was applied in the long-term stability tests for the determination of the mass bias and as a reference for the determination of the accurate magnesium isotopic composition of the ^{26}Mg-enriched solution applied. Details of the origin and preparation of the nutrient solution samples that were spiked with ^{26}Mg have been published elsewhere [28]. For the measurement of the isotopic ratios of ^{25}Mg/^{24}Mg and ^{26}Mg/^{24}Mg in the sample solutions, samples were diluted 200-fold and 2% subboiled nitric acid was added to them.

2.4. Measurement procedures

ICP-MS instrument optimization was carried out with the standard automatic optimization possibilities of the software with respect to the maximum signal intensities for magnesium. Further optimization was performed manually with 10 μg/L NIST SRM isotopic standard solution to achieve the lowest possible RSD of the isotopic ratios ^{25}Mg/^{24}Mg and ^{26}Mg/^{24}Mg. The mass bias for magnesium isotope ratio measurements was measured using isotopic standard solutions (NIST SRM 980) of different concentrations (1, 2, 5, 10, 20 and 50 μg/L).

Long-term stability of the ICP-MS was determined with 50 μg/L NIST SRM 980 magnesium isotope standard solution (the long-term stability of the ICP-QMS was tested for periods of up to 32 h by measurnig 10 aliquots in every period). Ten replicate measurements were performed from the above-mentioned solution and between measurements the instrument was flushed with 2% HNO_3 solution for 1 h. For sample introduction an autosampler was used.

For the study of the RSD of isotope ratio measurement at different magnesium concentrations, 1, 2, 5, 10, 20 and 50 μg/L solutions of the NIST SRM 980 standard were used. To determine the accuracy of the isotope ratio measurement, solutions of different isotopic composition were prepared from the NIST SRM 980 standard (1 μg/ml) and the ^{26}Mg-enriched laboratory standard (1 μg/ml). The ratio of the NIST SRM 980 standard to the ^{26}Mg-enriched spike was 2:3, 1:1 and 3:2 in these solutions with a final magnesium concentration of ~50 μg/L. For reverse isotopic dilution measurements, a 25μl sample was spiked with 250 μl of 1 μg/ml NIST SRM 980 magnesium isotopic standard and diluted to 10 ml with high-purity deionized water.

By the application of the isotope dilution technique the magnesium concentrations were calculated with the following equation (1):

$$Q_P = Q_T \cdot \frac{(T - X)}{(X - P)} \cdot \frac{m_P}{m_T} \qquad (1)$$

where Q_P is the element concentration in the sample, Q_T is the element concentration in the highly enriched tracer, T is the isotope ratio of two selected isotopes in the highly enriched tracer, P is the isotope ratio of these two selected isotopes in the sample, X is the isotope ratio of the two selected isotopes in the mixture, m_P is the atomic mass of the element in nature and m_T is the atomic mass of the isotopic-enriched element [3,18,23].

3. Results and discussion

3.1. Optimization of mass spectrometric method for the determination of Mg isotope ratios

To achieve precise and accurate results, the experimental parameters were optimized first with respect to the maximum ion intensities and second to the lowest RSD of the magnesium isotope ratios. The ion intensity maximum was observed at 0.85 L/min. For the analysis of small sample volumes the microconcentric Micromist nebulizer was applied with minicyclonic spray chamber for solution introduction to the ICP-MS. By using micronebulization the sample uptake rate was reduced (from ~1–2 ml/min for cross-flow nebulizer to ~0.1 ml/min for microconcentric nebulizer) and the measured ion intensity was increased (from ~12,000 cps/(μg/L) to ~25,000 cps/(μg/L) for aqueous magnesium standard solution).

Figure 1 shows the changes in isotope ratios and RSD in quadrupole ICP-MS using micronebulization as a function of nebulizer gas flow rate. Decreasing isotope ratios of ^{26}Mg/^{24}Mg and ^{25}Mg/^{24}Mg were observed when the nebulizer gas flow rate was increased (with a small increase at nebulizer gas flow rates higher than 0.87 L/min). The higher ^{26}Mg/^{24}Mg isotope ratio at low nebulizer gas flow rate could be explained by the nozzle separation effect, where the heavy isotopes are enriched in the central ion beam as described by Heumann et al. [4]. The lowest RSD was 0.26% for the ^{25}Mg/^{24}Mg isotope ratio at 0.85 L/min. For ^{26}Mg/^{24}Mg isotope ratio measurements 0.87 L/min nebulizer gas flow rate was selected. The RSD of the ^{26}Mg/^{24}Mg isotope ratio measurements varied between 0.37% to 0.59%. In Figure 2 the ^{25}Mg/^{24}Mg and ^{26}Mg/^{24}Mg isotope ratio values are shown as a function of radiofrequency power of the inductively coupled plasma. A small decrease of the measured isotope ratio was observed when the radiofrequency power was increased. In general lower magnesium isotope ratios (except for ^{26}Mg/^{24}Mg at radiofrequency power of 1200 and 1250 W) were measured compared to the certified ones. The RSD values were high at lower (1200–1325 W) radiofrequency power (up to 1.28%), and decreased with an increase in radiofrequency power. A possible explanation for this experimental result is the better plasma stability at higher radiofrequency power. Thus, the optimized nebulizer gas flow and radiofrequency power was different when the instrument was optimized for maximum ion intensity or lowest RSD in the isotope ratio (0.85 L/min and 1400 W versus 0.87 L/min and 1375 W, respectively).

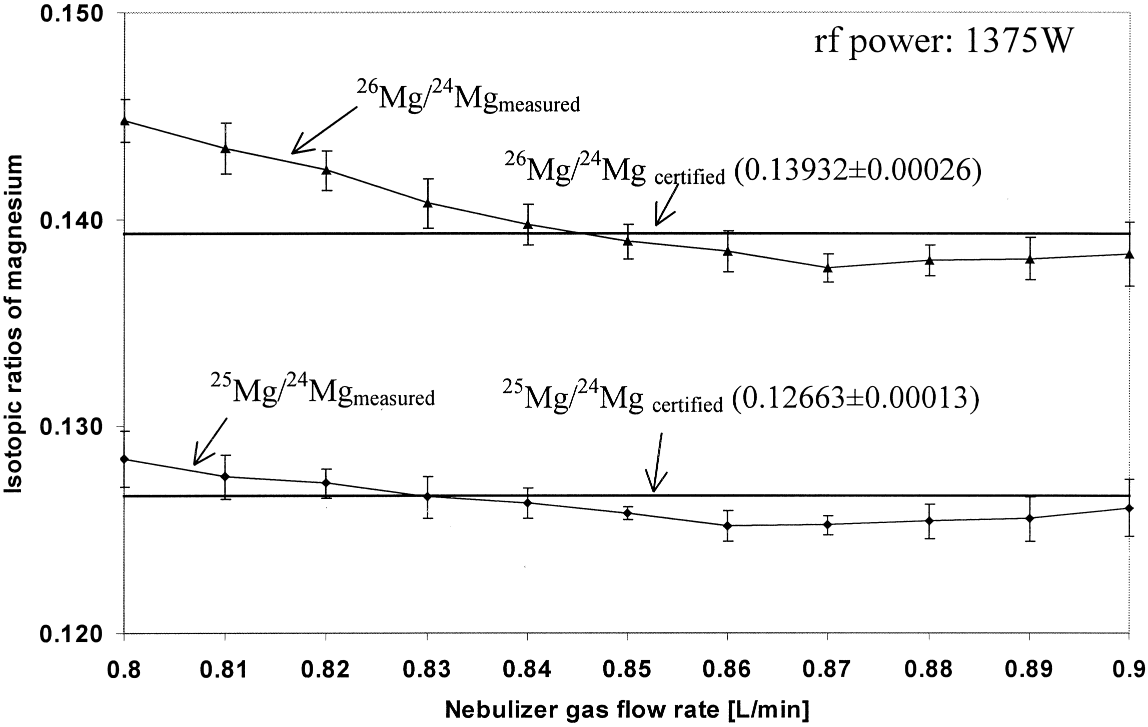

Fig. 1. Isotope ratios of magnesium versus nebulizer gas flow rate (50 μg/L NIST SRM 980 solution, radiofrequency power 1375 W).

3.2. Isotope ratio measurements of magnesium on isotope standard reference material and on ^{26}Mg-spiked nutrient solutions

In quadrupole-based ICP-MS the mass discrimination of ions due to the space-charge effect and nozzle-separation effect decreases with increasing mass. The mass discrimination of magnesium using the ICP-QMS Elan-6000 was studied in solutions of NIST SRM 980 isotope standard with different concentrations (1, 2, 5, 10, 20 and 50 μg/L) and the lowest values of mass discrimination of ^{26}Mg/^{24}Mg and ^{25}Mg/^{24}Mg found were 10.17% and 5.07%, respectively. These results are in agreement with the reported values [4].

The magnesium isotope ratios in the ^{26}Mg-enriched laboratory standard were determined by calibration against the NIST SRM 980 isotope standard. The determined isotopic ratios for the ^{26}Mg spike were ^{25}Mg/^{24}Mg $= 0.70849 \pm 0.00608$ and ^{26}Mg/^{24}Mg $= 58.89345 \pm 0.57373$. The calculated isotopic composition of the spike was 1.642% ^{24}Mg, 1.165% ^{25}Mg and 97.193% ^{26}Mg, which is different from the recommended values of 1.82%, 1.08% and 97.1%, respectively.

The effect of the concentration on the measured magnesium isotope ratios and relative standard deviations was studied using solutions of the NIST SRM 980 standard with concentrations ranging from 1 μg/L to 50 μg/L (Table 2). As expected, the RSD values of the magnesium isotope ratios decreased steadily with increasing Mg concentration. The observed RSD changes of the ^{25}Mg/^{24}Mg and ^{26}Mg/^{24}Mg isotope ratio from 1 μg/L to 50 μg/L solution concentration were 1.92% to 0.22% and 2.45% to 0.15%, respectively. Higher RSDs in the lower concentration range are due to the lower ion intensities, which means poorer ion counting statistics and lower signal-to-noise ratio. The accuracy of measured isotope ratios of ^{25}Mg/^{24}Mg and ^{26}Mg/^{24}Mg varied between 0.1–1.5% and 0.3–1.8%, respectively. Accuracy of 0.32% and 0.07% were reported, respectively, using double

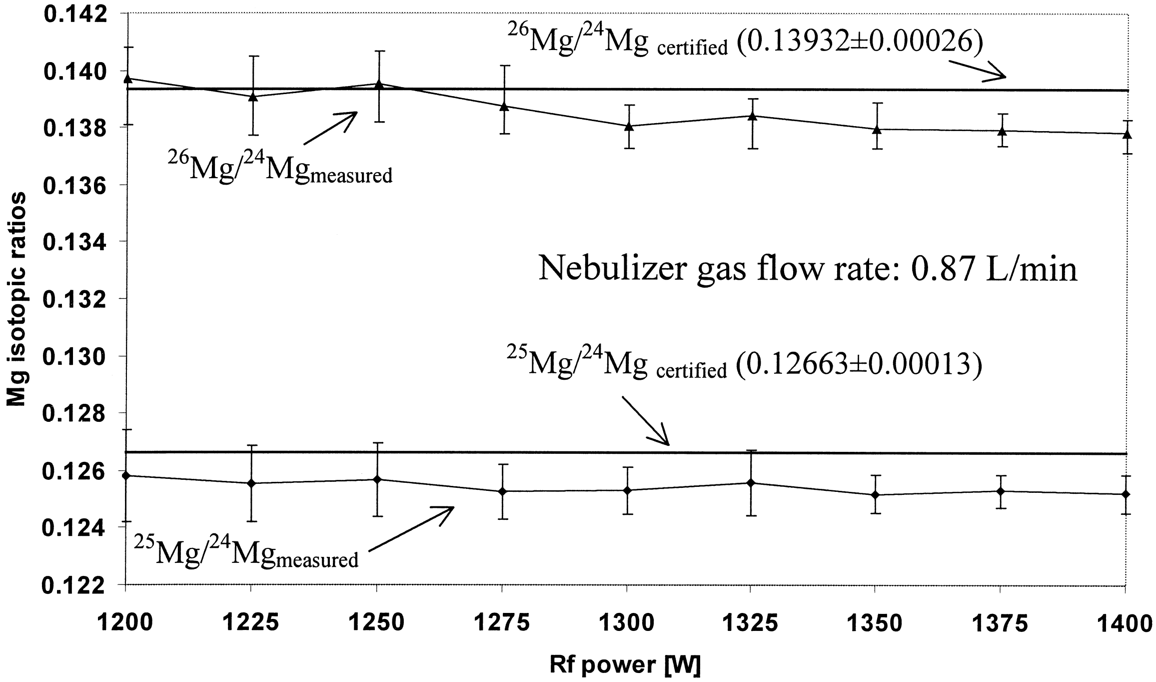

Fig. 2. Magnesium isotopic ratios versus radiofrequency power (50 μg/L Mg NIST SRM 980, nebulizer gas flow rate 0.87 L/min).

focusing ICP-MS (at mass resolution: $m/\Delta m = 3000$) and 50 μg/L NIST SRM 980 magnesium isotopic standard [7] and 0.04% RSD of $^{26}Mg/^{24}Mg$ isotope ratio ($m/\Delta m = 300$) and 500 μg/L Mg solution [29].

Furthermore, the short and long-term stability of the magnesium isotope ratio measurement was studied under optimum experimental conditions by using 50 μg/L NIST SRM 980 solution (Table 3). Slightly better short- and long-term stabilities were found in the case of $^{25}Mg/^{24}Mg$ isotope ratios: the short-term stability RSD ranged from 0.28% to 0.62% and the long-term stability RSD was 0.14%. For $^{26}Mg/^{24}Mg$ the measured short-term stability RSD range was 0.39% to 0.68% and the overall long-term stability RSD was 0.25%. Better long-term stabilities were reported for other elements like U ($^{235}U/^{238}U \sim 1$ with RSD of 0.05%) [18], but the results achieved here are at higher sensitivity, lower background and practially without disturbing interferences by molecular ions on masses 235u and 238u. In the present work high blank

Table 2
Measured isotope ratios in different magnesium concentrations of NIST SRM 980 solutions

	$^{25}Mg/^{24}Mg$		$^{26}Mg/^{24}Mg$	
Solution	Isotope ratio (± 1 RSD)	Accuracy (%)	Isotope ratio (± 1 RSD)	Accuracy (%)
1 μg/L	0.12721 (1.922%)	0.4	0.14185 (2.452%)	1.8
2 μg/L	0.12855 (1.457%)	1.5	0.14077 (1.561%)	1.0
5 μg/L	0.12769 (0.573%)	0.8	0.14102 (0.921%)	1.2
10 μg/L	0.12749 (0.478%)	0.6	0.14093 (0.766%)	1.2
20 μg/L	0.12690 (0.245%)	0.2	0.14048 (0.528%)	0.8
50 μg/L	0.12645 (0.222%)	0.1	0.13976 (0.153%)	0.3
Certified	0.12663		0.13932	

Table 3
Short-term and long-term stability of the measured isotope ratios in 50 μg/L NIST SRM 980 solution (nebulizer gas flow rate 0.87 L/min, radiofrequency power 1375W, $n = 10$)

	^{25}Mg/^{24}Mg			^{26}Mg/^{24}Mg		
Hours	Isotope ratio	RSD (%)	Accuracy (%)	Isotope ratio	RSD (%)	Accuracy (%)
3	0.12703 ± 0.00075	0.59	0.31	0.13989 ± 0.00095	0.68	0.41
6	0.12688 ± 0.00061	0.48	0.19	0.13936 ± 0.00074	0.53	0.03
9	0.12680 ± 0.00077	0.61	0.13	0.13909 ± 0.00087	0.63	0.17
12	0.12669 ± 0.00054	0.43	0.05	0.13897 ± 0.00085	0.61	0.25
15	0.12720 ± 0.00079	0.62	0.45	0.13991 ± 0.00061	0.44	0.42
18	0.12671 ± 0.00036	0.28	0.06	0.13949 ± 0.00069	0.50	0.12
21	0.12682 ± 0.00078	0.61	0.15	0.13954 ± 0.00057	0.41	0.16
24	0.12694 ± 0.00056	0.44	0.24	0.13967 ± 0.00055	0.39	0.25
27	0.12660 ± 0.00059	0.47	0.02	0.13985 ± 0.00066	0.47	0.38
30	0.12669 ± 0.00047	0.37	0.05	0.14001 ± 0.00058	0.42	0.49
Average	0.12684 ± 0.00018	0.14	0.17	0.13958 ± 0.00036	0.25	0.38
Certified	0.12663 ± 0.00013			0.13932 ± 0.00026		

values in ICP-QMS on masses 24u, 25u and 26u were found (25000 cps, 2000 cps and 8000 cps, respectively) because of interferences from molecular ions ($^{12}C_2^+$, $^{12}C_2{}^1H^+$, $^{12}C^{13}C^+$, $^{12}C^{14}N^+$, etc.). Increasing RSDs of the measured isotope ratios were observed when the magnesium concentrations were decreased

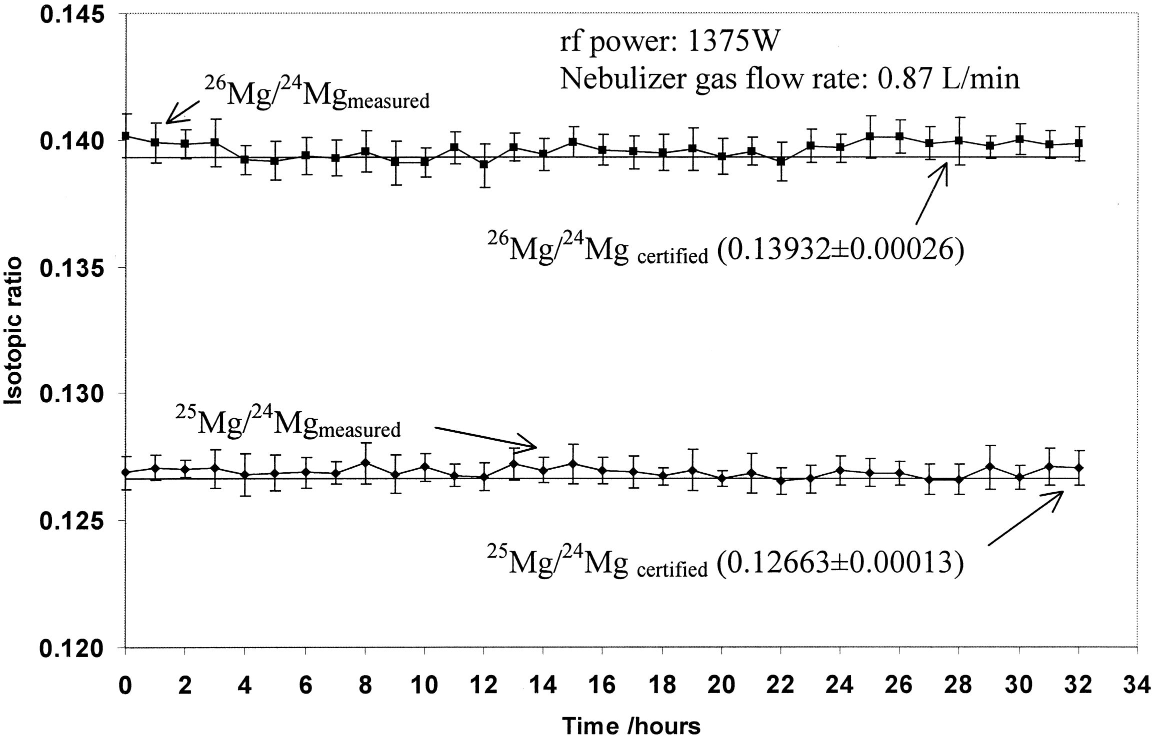

Fig. 3. Long-term stability of magnesium isotopic ratios (50 μg/L NIST SRM 980).

Table 4
Results of the different isotopic mixtures ($n = 10$)

Mixtures			$^{25}Mg/^{24}Mg$		$^{26}Mg/^{24}Mg$	
1 μg/g NIST SRM 980	1 μg/g ^{26}Mg-spike	End volume	Estimated	Measured	Estimated	Measured
200 μL	300 μL	10 mL	0.13204	0.13381 ± 0.00020	0.75363	0.76526 ± 0.00155
250 μL	250 μL	10 mL	0.13503	0.13743 ± 0.00011	1.05582	1.07495 ± 0.00152
300 μL	200 μL	10 mL	0.13945	0.14185 ± 0.00011	1.50328	1.54143 ± 0.00067

because of the disturbing interferences. In Figure 3 the long-term stability of magnesium isotope ratio measurements are demonstrated. The determined magnesium isotope ratios were similar during the 32 h of the long-term stability measurement with only small instability of the inductively coupled plasma, which is demonstrated by the RSD of the individual results. The measured isotope ratios were $^{25}Mg/^{24}Mg = 0.12684 \pm 0.00018$ and $^{26}Mg/^{24}Mg = 0.13958 \pm 0.00036$, which are in agreement with the certified values (0.12663 ± 0.00013 and 0.13932 ± 0.00026, respectively). The accuracy of the individual measurements of the $^{25}Mg/^{24}Mg$ and $^{26}Mg/^{24}Mg$ isotope ratios varied between 0.02-0.45% and 0.03-0.49%, and the overall accuracy of the long-term stability measurement was 0.17 % and 0.38%, respectively.

Furthermore, the accuracy of the isotope ratio measurement of magnesium was studied by isotope mixtures with different isotopic composition using the NIST SRM 980 magnesium isotope standard solution and the ^{26}Mg-enriched spike solution. In these mixtures the $^{25}Mg/^{24}Mg$ isotope ratio was nearly constant, and the $^{26}Mg/^{24}Mg$ isotope ratio varied from 0.75 to 1.5. These results are summarized in Table 4.

The results of the magnesium isotope ratio measurements of some nutrient solution samples are shown in Table 5. In the investigated samples the $^{26}Mg/^{24}Mg$ isotopic ratio values obtained were considerably higher, and the $^{25}Mg/^{24}Mg$ isotope ratio values were slightly higher than the isotope ratios found in a sample with natural isotope abundance.

3.3. Results of magnesium concentrations determined by reverse isotope dilution technique

The isotopic composition of magnesium in the plant nutrient solutions investigated (Table 5) was quite different than the natural composition due to spiking with high enriched ^{26}Mg in the tracer experiments. To determine the Mg concentration in these ^{26}Mg-spiked nutrient solutions, samples were doped with NIST SRM 980 magnesium isotopic standard with natural isotopic composition. The magnesium concentration in these doped samples was measured with reverse isotope dilution.

The quantitative measurement results using the reverse isotope dilution technique on magnesium are compared in Table 6 to the concentrations measured with ICP-OES and with ICP-MS using external calibration. The observed RSD of the different measurements is the lowest in the case of reverse isotope dilution (0.01% to 0.06%), followed by ICP-MS with external calibration (0.12% to 0.21%), and the highest RSD values were found in the case of ICP-OES (0.4% to 0.8%). In general, the average concentrations of the reverse dilution measurement are higher than the

Table 5
Results of isotope ratio measurements of magnesium in selected nutrient solution samples

Sample ID	$^{25}Mg/^{24}Mg$	$^{26}Mg/^{24}Mg$
#5	0.22254 ± 0.00126	9.67318 ± 0.04256
#7	0.26637 ± 0.00162	14.39059 ± 0.07629
#18	0.48779 ± 0.00346	37.38061 ± 0.16821
#20	0.46058 ± 0.00317	34.60692 ± 0.14189
#23	0.39516 ± 0.00205	27.48922 ± 0.09896
Natural sample	0.12695 ± 0.00033	0.14183 ± 0.0034

Table 6
Quantitative measurement results of some selected samples by ICP-OES, ICP-MS with external calibration and ICP-MS with reverse isotope dilution technique (concentrations in μg/g)

	ICP-MS		
Sample	Reverse isotope dilution	External calibration	ICP-OES
#5	8.97 ± 0.02	8.71 ± 0.14	7.8 ± 0.4
#7	15.95 ± 0.04	15.31 ± 0.12	15.3 ± 0.8
#18	14.61 ± 0.06	14.21 ± 0.13	13.2 ± 0.7
#20	16.54 ± 0.06	16.56 ± 0.21	15.3 ± 0.8
#23	9.54 ± 0.02	9.45 ± 0.13	8.8 ± 0.5

ICP-OES results. The agreement with the ICP-MS results using external calibration is better for most samples than with the ICP-OES method, which could indicate a systematic error in the ICP-OES measurements. Another possible explanation is that the magnesium concentration was too low for accurate measurement with ICP-OES due to the low sample volume and high dilution factor. For sample 7 better agreement was found between the ICP-OES result and the concentration measured by ICP-MS with external calibration.

4. Conclusions

It has been shown that an ICP-QMS can be applied successfully for precise isotope ratio measurements of magnesium at a low concentration level. Due to the good precision in short-term and long-term stability of the magnesium isotope ratio measurements, the reverse isotope dilution method developed by us was successful for determination of magnesium concentration in ^{26}Mg-enriched nutrient solution samples. The concentration values determined were generally in good agreement with the values obtained by ICP-MS using external calibration, but were higher than the ICP-OES results.

In future work the method will be applied for the precise isotope analysis of small amounts of solid biological samples after closed-vessel microwave digestion. The required sample amount will be further decreased by using a direct injection high-efficiency nebulizer (DIHEN) for sample introduction, and the method will be applied for very small plant tissue samples for the determination of tissue-specific isotope distributions in the plant.

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