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Low level determination of gallium isotopes by ICP-QQQ

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Abstract

Determination of low concentrations of Ga in environmental or biological samples can benefit from interference free measurement of both Ga isotopes. Unfortunately, both isotopes have potential interferences, i.e doubly charged Ba at m/z 69 and MnO at 71. Analysis using collision and reaction gases by ICP-QQQ as an alternative to HR-ICP-MS is investigated here using conventional nebulization and a desolvating nebulizer. Analysis at m/z 71 is not appreciably affected by MnO at 200 $\mu\text{g/l}$ Mn or in either water reference material; excellent detection limits of < 0.1 ng/l were obtained for He, H_2 , or on-mass O_2 and NH_3 gas modes. Analysis of Ga at m/z 69 was severely affected by doubly charged Ba across all gas modes except +17 mass-shift (i.e. 69 – 86) NH_3 gas mode. Despite Ga being only 1–2% reactive at the 69–86 mass shift, the doubly-charged interference was not mass-shifted and detection limits of < 1 ng/l and precise and accurate quantification of two water reference materials and nine natural water samples were achievable for this analysis mode.

Introduction

Gallium occurs in group 13 of the periodic table, its atomic weight is 69.72 and it has two isotopes, 69 and 71, of relative abundance 60.11 and 39.89. Gallium has chemical similarities to Al and is mostly mined as a by-product of bauxite mining¹. Commercial use of Ga has dramatically increased in the late 20th century because of the use of gallium arsenide, GaAs, as a semiconductor¹. Consequently, efforts have been made to evaluate the carcinogenicity of GaAs², exposure to Ga through food³ and Ga levels in waste-impacted streams⁴. Gallium has also found use in pharmaceutical drugs⁵ and affinity tags⁵ and methods have been developed for Ga analysis of biological fluids.⁶ Because of the chemical similarity between Ga and Al and the inclusion of Ga in Al-containing minerals, geochemists have utilized Ga/Al ratios in natural waters to assess rock weathering, with the dissolved phase being enriched in Ga/Al relative to the solid phase^{7–9}.

The high sensitivity of ICP-MS makes it the preferred method for analysis of Ga in environmental and biological media^{4–6, 10}. However, Ga analysis is challenging because it is usually present at low concentrations and in the presence of high concentrations of interfering ions, notably Ba^{2+} that interferes with Ga at m/z 69 and MnO that interferes at m/z 71. Sector field-ICP-MS operated at higher mass resolution could potentially provide

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Conflicts of interest

There are no conflicts to declare.

analysis of the Ga isotopes free from doubly-charged or oxide interferences; resolution of Ba²⁺ at m/z 69 and MnO at m/z 71 from the Ga isotopes require ca 2600 and 8500 resolution which is within the capabilities of sector field-ICP-MS. However, ion transmission, and therefore analyte sensitivity, is greatly reduced in going to medium and high-resolution settings effectively raising the detection limits for the target analyte. Here we report on the use of reaction-cell ICP-QQQ to measure both Ga 69 and 71 in natural samples without polyatomic or double-charge interferences. Precise and accurate analysis of both Ga isotopes is a pre-requisite for isotope dilution analysis, but it is also very useful for external calibration quantification, where checking that the measured isotopic abundance reflects the known natural abundance gives an additional level of confidence that the true concentration is being determined.

Experimental

Gallium analysis was carried out on an Agilent 8900 ICP-QQQ, using no-gas, and He, H₂, O₂, and NH₃ (10% in Ar) collision/reaction gases. The analysis was performed with a conventional spray chamber and, to further enhance instrument sensitivity, an APEX desolvating system. To assess which adducts, if any, are formed with Ga and NH₃ reaction gas a product ion scan was performed using a 1 µg/l Ga solution, an identical scan, i.e. m/z 69 and all potential NH_x^y adducts was performed using a 100 µg/l Ba solution. Gallium is relatively unreactive towards NH₃ and only the +17 adduct (69 – 86) was formed to any appreciable extent, therefore only the on-mass and +17 mass-shifted adducts were included in the analytical method for NH₃. For O₂ reaction gas Ga is not mass shifted and remains essentially 100% on-mass, therefore only the O₂ on-mass data is presented here. The final ICP-QQQ operating conditions are described in Table 1.

The instrument was calibrated with a blank and six calibration standards from 1 ng/l – 50000 ng/l and the calibration was verified by a 2nd source standard. Yttrium was added throughout as an internal standard and monitored in all gas modes. To assess the double charge and oxide interferences from Ba and Mn, 200 µg/l single element solutions of each were run and the effective concentrations of Ga at each gas mode were measured. Two water reference materials, TM 9.2 and TMDA 64.3 (Environment and Climate Change Canada, Ottawa, Canada) that have certified values for Ga and contain Ba and Mn, were also run to assess accuracy. Nine natural water samples, 3 commercial mineral waters, local tap water, a New Hampshire surface water and four well water samples were run with the optimized method to assess its applicability to real world samples.

Results and Discussion

Preliminary mass scans showed that Ga was not mass shifted in O₂ mode and was generally unreactive in NH₃ mode with only 1 – 2% mass shift by 17 amu i.e transitions 69 – 86, 71 – 88. However, because doubly-charged interference for Ba was not mass shifted in NH₃ mode this suggested that the +17 mass shift could still be viable to detect Ga 69 without double-charged Ba interference and despite the low percent of Ga undergoing the mass shift. The flow of NH₃ was varied and the response of Ga and Ba on mass and +17 mass shifted was monitored. A flow rate of 50% was determined to be optimum (Figure 1).

The figures of merit for the conventional sample introduction system and the APEX are shown in Table 2. Detection limits were generally very good (0.02 – 1 ng/l) across all analytical modes except mass shift 69–86 in NH₃ mode for the Scott spray chamber where the DL was 3.25 ng/l. However, the DL for this mass shift was significantly improved, to 0.28 ng/l, by using the APEX, which increased sensitivity by a factor of 5 while the background signal did not increase. Use of the Apex did not otherwise improve detection limits in other analysis modes because blank signal also increased. Detection limits were generally higher at m/z 69 despite this being the more abundant mass due to the increased background signal at this mass. ‘False positive’ concentrations for Ga at m/z 69 in the presence of Ba were significant across all gas modes except the NH₃ mass shifted mode. Apparent Ga (m/z) concentrations of 64 and 151 µg/L for 200 µg/L Ba solution were measured in He mode again illustrating that doubly-charged interference is exacerbated not mitigated in He mode. In general, false positives were approximately twice as high for the APEX, which may be a result of increased double-charged formation, enhanced sensitivity or increased carry-over from the previous sample (TMDA 63.2, Ga concentration 50 µg/L). Because the Ba²⁺ did not react with NH₃, essentially no false positive Ga concentration was measured at m/z 69 for the 69–86 transition. The reported 2 ng/L (Scott) and 7.75 ng/L (APEX) for the 200 ppb Ba solution may be due to residual carryover from TMDA 64.3, or actual Ga contamination of the primary Ba stock solution. There was essentially no appreciable MnO interference on Ga at m/z 71 for any analysis mode and optimum detection limits of 0.02 ng/L were calculated at m/z 71 in H₂ mode. Clearly, m/z 71 would be the preferred measurement mass for external calibration. Gallium at m/z 69 was significantly over-estimated in the two reference water samples in all gas modes except NH₃ 69–86 mass shift where recoveries were 104 and 97, and 98 and 91 % for conventional and Apex sample introduction systems respectively. Recoveries for Ga at m/z 71 ranged from 93–104 % across the different gas modes. Mass bias of m/z 69/71 measured across calibration standards > 40 nl/L Ga and TMDA 64.3 and TM 9.2 were $-8.0\% \pm 0.75\%$ and $-8.0\% \pm 0.36\%$ for conventional and APEX sample introduction systems for the NH₃ +17 mass shift. Clearly, after appropriate mass bias correction, the m/z 69 mass could be used for quantitation or isotope dilution when using the NH₃ +17 mass shift.

The measured Ga concentrations in NH₃ mode at m/z 69 and 71 both on-mass (OM) and mass-shifted (MS) for 9 natural water samples are shown in Table 3. In 8 of the 9 samples the measured Ga concentration at m/z 69 OM is clearly overestimated due to Ba²⁺ interference. However, the measured Ga concentrations for m/z 69 MS and m/z 71 OM and MS are in very good agreement in 8 of 9 samples which strongly suggests that these are good estimates of the true Ga concentration. Only in sample 1, a hard mineral water, is the CV of these 3 Ga concentrations > 10%, which suggests that there may be an unknown Ga interference at m/z 69 MS for high TDS samples and low Ga concentration. However, the apparent Ga concentrations for m/z 69 MS and m/z 71 OM and MS for the other 8 samples were in excellent agreement with an average CV of 2%, even though 5 of these samples have Ga concentrations of < 5 ng/l.

Conclusions

Gallium concentration in natural water samples ranges from $< 5 \text{ pM}$ – 100 pM and past analytical methods have used preconcentration via precipitation or resin adsorption followed by HR-ICP-MS¹¹ or GFAAS⁹. In this study, analysis by ICP-QQQ using NH_3 and H_2 enabled 1 ng/l detection limits for Ga 69 and sub-ng/l detection limits for Ga 71 respectively thus allowing for low level isotope dilution analysis or the use of both Ga isotopes in external calibration for confirmation of low Ga concentrations in environmental samples.

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Figure 1.
Signal response for on-mass and mass shift (+17) at m/z 69 for 1 ug/l Ga and 200 ug/l Ba solutions.

Table 1

Selected ICP-MS operating conditions. Other parameters were auto-tuned for each gas mode

	Scott	APEX
RF Power (W)	1550	1550
sample depth (mm)	8	8
Neb gas flow (l/min)	1	1
make-up gas (l/min)	0.13	0.1
Extract 1 (V)	−12	−12
Extract 2 (V)	−210	−185
Omega Bias (V)	−130	−115
Omega lens (V)	10.8	10.2
He flow(ml/min)	5	5
H2 flow(ml/min)	7	7
O2 flow (%)	25	25
NH3 flow (%)	50	50

Table 2

Summary of detection limits, doubly-charged and oxide interference, and Ga recoveries in all gas modes using ICP-QQQ.

	No gas		hydrogen		helium		oxygen		Ammonia	
	SQ	MS/MS	on mass	SQ	MS/MS	on mass	MS/MS	on mass	MS/MS	mass shift (+17)
Gallium m/z 69										
<i>Scott spray chamber</i>										
Detection limits (ng/l)	0.17	0.14	0.127	0.20	0.12	0.20	0.12	0.20	0.12	3.25
% Recovery TM 9.2	224%	179%	832%	213%	148%	213%	148%	213%	148%	104%
% Recovery TMDA 63.2	130%	123%	288%	144%	117%	144%	117%	144%	117%	97%
200 ppb Ba: apparent Ga concentration (ng/l)	10841	6968	64339	14411	4182	14411	4182	14411	4182	2
200 ppb Mn: apparent Ga concentration (ng/l)	1.57	1.32	6.57	1.42	0.73	1.42	0.73	1.42	0.73	BDL
<i>Apex desolvating nebulizer</i>										
Detection limits (ng/L)	0.78	0.39	1.16	0.16	0.31	0.16	0.31	0.16	0.31	0.28
% Recovery TM 9.2	246%	221%	1304%	280%	168%	280%	168%	280%	168%	98%
% Recovery TMDA 63.2	134%	125%	432%	143%	116%	143%	116%	143%	116%	91%
200 ppb Ba: apparent Ga concentration	18371	14912	151462	22439	10064	22439	10064	22439	10064	7.75
200 ppb Mn: apparent Ga concentration	22.46	6.20	29.36	4.14	1.87	4.14	1.87	4.14	1.87	0.68
Gallium m/z 71										
<i>Scott spray chamber</i>										
Detection limits (ng/L)	0.12	0.02	0.63	0.04	0.08	0.04	0.08	0.04	0.08	2.02
% Recovery TM 9.2	102%	102%	103%	103%	102%	103%	102%	103%	102%	104%
% Recovery TMDA 63.2	100%	97%	97%	104%	101%	104%	101%	104%	101%	97%
200 ppb Ba: apparent Ga concentration (ng/l)	5	5	5	3	2	3	2	3	2	1
200 ppb Mn: apparent Ga concentration (ng/l)	2.57	0.53	0.86	3.47	0.42	3.47	0.42	3.47	0.42	BDL
<i>Apex desolvating nebulizer</i>										
Detection limits (ng/l)	0.17	0.13	0.21	0.08	0.20	0.08	0.20	0.08	0.20	0.83
% Recovery TM 9.2	97%	98%	83%	98%	94%	98%	94%	98%	94%	98%
% Recovery TMDA 63.2	93%	93%	95%	92%	93%	92%	93%	92%	93%	93%
200 ppb Ba: apparent Ga concentration (ng/l)	29.95	19.29	9.27	14.69	5.28	14.69	5.28	14.69	5.28	5.40
200 ppb Mn: apparent Ga concentration (ng/l)	4.32	1.83	1.48	1.90	0.64	1.90	0.64	1.90	0.64	0.60

Table 3

Apparent Ga concentration in nine natural water samples in on-mass and mass shift NH_3 gas mode.

Sample type	Apparent Ga concentration (ng/l $\pm$ SD)			
	m/z 69 OM	m/z 69 MS	m/z 71 OM	m/z 71 MS
mineral water	77.23 ± 18.1	3.39 ± 0.96	1.67 ± 0.55	2.03 ± 0.65
mineral water	23.92 ± 0.20	2.04 ± 0.27	2.03 ± 0.03	1.98 ± 0.12
mineral water	384.01 ± 6.14	370.42 ± 7.4	367.89 ± 5.6	368.97 ± 8.09
municipal water	187.57 ± 4.38	2.25 ± 0.24	2.03 ± 0.05	1.98 ± 0.24
river water	82.07 ± 0.37	3.67 ± 0.18	3.92 ± 0.06	3.74 ± 0.1
ground water	239.23 ± 7.14	9.73 ± 0.38	9.70 ± 0.28	9.75 ± 0.21
ground water	145.17 ± 3.25	4.05 ± 0.32	4.06 ± 0.11	3.95 ± 0.32
ground water	78.67 ± 1.56	14.96 ± 0.39	15.03 ± 0.22	14.80 ± 0.33
ground water	634.23 ± 10.07	3.31 ± 0.22	3.43 ± 0.11	3.35 ± 0.28