Atomic Spectroscopy

Article

Accurate Determination of Trace Gallium in Antarctic Terrestrial Flora using Electrothermal Atomic Absorption Spectrometry

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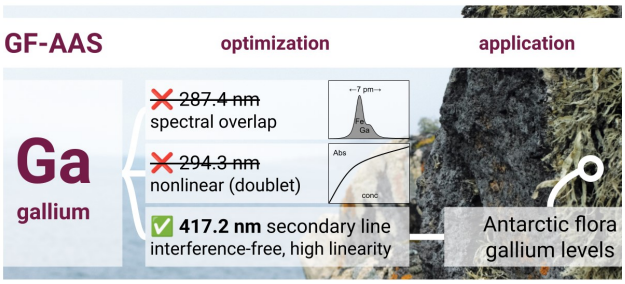
ABSTRACT: Gallium is a technology-critical element whose concentration increases owing to industrial activity. To study anthropogenic contamination in maritime Antarctica (Nelson Island, South Shetland Islands), it was necessary to develop an analytical method to determine the trace Ga content in Antarctic flora. The determination of Ga using electrothermal atomic absorption spectrometry (ETAAS) is a seemingly routine analytical task; however, the commonly used atomic lines of 287.4 nm and 294.4 nm appear to be unsuitable for analytical use. In this study, the fundamental aspects of Ga determination were investigated, and an atomic line at a wavelength of 417.2 nm was recommended for the analysis of environmental samples. The Ga content in mosses, lichens, mushrooms, and grass samples from Antarctica are published here for the first time. Based on the Ga content of lichens as biomonitors of atmospheric pollution, it can be assumed that contamination of the studied locality through atmospheric deposition is low.



INTRODUCTION

Gallium is a technology-critical element whose concentration is increasing in the environment; however, its natural background has been relatively little explored. The main anthropogenic sources of Ga are the combustion of coal, coal fly ash, and the production of aluminum,[1-3] where Ga is produced as a byproduct during bauxite processing. Global Ga flux is described in a review by Yuan et al.[3] Because of its semiconducting properties, Ga is widely used in electronic components, most commonly in GaAs and GaN compounds. Other applications of Ga are found in radiomedicine, in dentistry, in the manufacture of lasers, in liquid crystal displays, and in microwave generators.[1,4-6] The GaP, GaAs, and AlGaAs compounds used in the semiconductor industry are toxic and carcinogenic in the form of airborne particulates.[4,7-9] Ga accumulation in the human body can cause both chronic and acute damage to the lungs, kidneys, and reproductive organs.[10,11] Furthermore, Ga interferes in iron metabolism and affects the immune system.[7] A summary of the toxic effects of Ga compounds inhalation (an occupational hazard in the semiconductor industry) is given in the review by Tanaka[12] and in other works.[4,13]

The Ga content in the Earth's crust ranges from 15 to 19 mg kg^{-1}.[5] The Rudnick and Gao[14] stated that the Ga content in the upper crust is 17.5 mg kg^{-1}. Ga is associated with feldspars; therefore, it is positively correlated with the clay minerals in soils. It is also correlated with aluminum, oxo-hydroxides of iron, and manganese,[1,2] due to its ionic radius. The Ga content in soils can exceed contents in the Earth's crust due to its association with aluminum;[5] therefore, its contents in soils can reach up to 70 mg kg^{-1}.[6] In the vicinity of mines and metal processing facilities, hundreds of mg kg^{-1} of Ga in soils appear.[10] The semiconductor industry also presents a risk of groundwater contamination.[15] Due to Ga accumulation in some plant species, contamination of the food chain is possible. For example, the transport of Ga from the soil to rice plants was described by Chen et al.[10] Published Ga

content in plants ranging from 3 to 30 mg kg^{-1}. The highest published content of Ga in lichens is approximately 60 mg kg^{-1}; up to 30 mg kg^{-1} can be found in bryophytes.[5] Because of this accumulation potential, lichens and bryophytes are often used for air pollution biomonitoring.[11,16,17] An example of such use is presented in the work of Berg and Steinnes,[18] where an aluminum smelter was identified as a source of Ga contamination using the moss *Hylocomium splendens*.

The most commonly used techniques for determining Ga in the environment are electrothermal atomic absorption spectrometry (ETAAS) and flame atomic absorption spectrometry (FAAS). Other analytical techniques used for Ga determination include inductively coupled plasma mass spectrometry (ICP-MS), UV/VIS spectrometry, neutron activation analysis, and X-ray emission.[4,19] Determination of the trace Ga content by means of ETAAS (with or without preconcentration) is routinely used in environmental analysis.[1,6,19,20] Discrepancies with respect to the suitability of particular Ga atomic lines or the use of a matrix modifier are evident. The determination of Ga is performed at the 294.4 nm atomic line[1,20] and at the 287.4 nm atomic line.[6,19] To determine Ga, it is convenient to coat the platform of the atomizer with carbide-forming elements such as W, Ta, Zr, or Mo,[19] although Ga itself does not form carbides.[21] A multiple increase in the signal was observed in the case of a graphite platform coated with W or Zr. The atomization mechanism of Ga involves the decomposition of solid Ga_2O_3 into gaseous Ga_2O at temperatures above 1000 °C. The formation of gaseous Ga_2O between 1000 °C and 1500 °C accounts for the main loss of sensitivity in Ga determination. Furthermore, gaseous Ga_2O is reduced to gaseous Ga at the graphite wall of the atomizer, which can cause a double peak.[20] Thus, the pyrolysis temperature is crucial for the loss of gaseous Ga before the atomization step.

The aims of this study were primarily to clarify the choice of a suitable spectral line for determining Ga using ETAAS with a line or continuous source of radiation and to develop an analytical method. Currently, there are inconsistencies in the recommendations regarding Ga spectral lines between manufacturers and AAS authorities. Therefore, we aimed to identify appropriate settings for environmental applications. Our focus was on applying the developed method to samples of Antarctic flora to establish the background levels of Ga in maritime Antarctica. As the use of technology-critical elements such as Ga is expected to increase, knowing their current environmental concentrations is of utmost importance.

EXPERIMENTAL

Location and samples. Since the discovery of Antarctica, the South Shetland Islands of Antarctica have been exposed to the long-term influence of anthropogenic activities. Nelson Island has a relatively pristine environment compared with the other islands of this archipelago, as it does not host any permanent polar stations. The Stansbury Peninsula (62°15 S, 58°59 W) in the northwest of Nelson Island accounts for 8 km^2 of deglaciated terrain, which provides an occasional refuge for seabirds and mammals. Overall, it is an area with Antarctic soils that are poor in organic matter and are formed mainly on basaltic volcanic rocks.[22]

Samples of the lichens *Usnea antarctica* (n=27), *Usnea aurantiaco-atra* (n=23), and *Ramalina terebrata* (n=4); the mosses *Sanionia uncinata* (n=15), *Polytrichum sp.* (n=3), and *Bryum pseudotriquetrum* (n=3) and their mixtures (n=8); the grass *Deschampsia antarctica* (n=5); and the mushrooms *Arrhenia antarctica* (n=6) and *Arrhenia cf. Lilacinicolor* (n=1) were collected on Stansbury Peninsula. A more detailed description of the collection of these samples, including a map of the locality, is provided in a previous publication from this Antarctic expedition.[23]

Preparation of samples and reagents. The samples were prepared according to the procedure described in Zvěřina et al. (2024).[23] Briefly, in a clean laboratory, the samples were rinsed with deionized water, dried, and homogenized by grinding. Digestion in nitric acid was performed using an UltraWAVE microwave mineralizer (Milestone, Italy). Ten experimental blanks were prepared alongside the samples.

A Ga standard solution was prepared by dissolving solid Ga_2O_3 (The British Drug Houses Ltd., England) in hot HCl (Suprapure, 30%, Ga < 0.0000005%, Merck, Germany). A mixed Pd/$Mg(NO_3)_2$ matrix modifier prepared from Pd modifier (10 g/L, Merck, Germany) and $Mg(NO_3)_2.6H_2O$ (Suprapure, 99.99%, Merck, Germany) was used for Ga determination by ETAAS.

Instrumentation. Two atomic absorption spectrometers with graphite furnaces were employed; an Analyst 600 (PerkinElmer, USA) equipped with a line radiation source and a ContrAA 800G (Analytik Jena, Germany) equipped with a continuous radiation source. An Analyst 600 atomic absorption spectrometer with a longitudinal Zeeman-effect background correction was equipped with a solid-state detector. The radiation source was a Ga hollow cathode lamp filled with Ne and the lamp current was set to 15 mA. Slits of 0.2 nm and 0.7 nm were used. Three wavelengths were used to determine the Ga: 287.4 nm, 294.4 nm, and 417.2 nm. An advanced platform graphite tube with an End-Cap (PerkinElmer, USA) was used for Ga determination.

A ContrAA 800 G high-resolution continuum source atomic absorption spectrometer was used to study the spectral surroundings of all monitored Ga atomic lines. The ContrAA 800 G was equipped with a CCD detector. A xenon short-arc lamp was used as the radiation source.

Table 1. Temperature program for Ga determination

Step	Temperature (°C)	Ramp Time (s)	Hold Time (s)	Ar Flow (mL min^{-1})
Drying 1	110	1	60	250
Drying 2	130	15	30	250
Pyrolysis	900	10	30	250
Atomization	2400	1	5	0
Cleaning	2600	1	2	250

Fig. 1 Pyrolysis and atomization curves for Ga.

Fig. 2 Ga calibration curves for 287.4 nm, 294.4 nm, and 417.2 nm at 0.7 nm slit (a), and calibration curve for 417.2 nm at 0.2 nm slit (b).

Analytical procedures. Three atomic lines of Ga and their spectral surroundings were investigated to determine the concentration of Ga in the real samples. The 287.424 nm atomic line is commonly recommended by the manufacturer (PerkinElmer, USA) and frequently appears in the literature.[6,19] The same sensitivity is also shown for the 294.364 nm atomic line, which is accompanied by a nearby 294.417 nm atomic line with a relative sensitivity of 11% (compared to the most intense line). However, this doublet cannot be distinguished using conventional line-source atomic absorption spectrometry. Thus, these lines together have seemingly higher sensitivity for spectrometers with a line radiation source when a slit of 0.2 nm or wider is used. The third spectral line with a sensitivity of 67% is the 417.204 nm atomic line, which has the benefit of being located in a spectral region that is minimally disturbed by the molecular absorption bands.

First, the addition of the matrix modifier and the temperature program of the graphite furnace were optimized for Ga determination. The pyrolysis and atomization curves of the Ga standard with a concentration of 40 µg L^{-1} are shown in Fig. 1. The optimized temperature program for the graphite furnace is listed in Table 1. The determination of Ga was performed using 20 µL of standard/sample dosed on the graphite platform together with 30 µL of Pd/$Mg(NO_3)_2$ matrix modifier. Thus, the resulting amount of modifier was 15 µg Pd and 9 µg $Mg(NO_3)_2$ per one firing.

The calibration dependencies of Ga standards with concentrations of up to 40 µg L^{-1} were determined for all three spectral lines using a slit of 0.7 nm as recommended by the manufacturer (Fig. 2a). Subsequently, the linear range of Ga determination for the calibration standards was observed at the wavelength of 417.2 nm and with a slit of 0.2 nm (Fig 2b). Calibration for the determination of Ga in real Antarctic flora samples was performed using the standard addition method at a wavelength of 417.2 nm and with a slit of 0.2 nm.

A ContrAA 800 G spectrometer was used to monitor the spectral surroundings of all three atomic lines in order to select the appropriate atomic line for the determination of Ga using a spectrometer with a line radiation source. This technique also served as a reference method.

Three parallel analyses were performed for each sample and experimental blank. The limits of detection (LOD) and quantification (LOQ) were calculated as three and ten times the standard deviation of the blank, respectively, divided by the slope of the calibration curve. The repeatability of Ga determination was monitored for three consecutive days using calibration standards and real samples. The accuracy of determination was determined by the spiking the samples with Ga standards. Unfortunately, no certified reference material comprising a plant matrix with a certified Ga content is available.

Fig. 3 Spectral surroundings of 287.424 nm, 294.364 nm, and 417.204 nm lines for *Sanionia uncinata* moss sample observed with high-resolution continuum source AA spectrometer. The section in Fig. 3a shows overlap of Fe and Ga lines using Fe 10 mg L^{-1} and Ga 10 μg L^{-1} standards.

Visualization of the data and statistical analyses were performed using OriginPro software.

RESULTS AND DISCUSSION

Determination of Ga by ETAAS. The accurate determination of Ga in environmental samples by ETAAS with a line radiation source depends on the following key factors: appropriate pyrolysis temperature, use of a matrix modifier, and selection of the appropriate spectral line.

At first glance, the pyrolysis curve of Ga (Fig. 1) did not indicate a maximum pyrolysis temperature of 900 °C with regard to the stable signal up to 1500 °C. The theoretical behavior of gallium oxide at high temperatures is decisive in this case, as was described in the work of Imai et al.[20] A pyrolysis temperature of 900 °C was chosen due to potential analyte losses at higher temperatures. Broadening of the Ga peak occurs at an atomization temperature below 2300 °C; atomization temperatures between 2500 and 2600 °C do not improve the analytical signal but wear out the atomizer. A sufficient amount of a matrix modifier is required to determine Ga. For the Pd/$Mg(NO_3)_2$ matrix modifier used in this procedure, the use of 15 μg Pd and 9 μg $Mg(NO_3)_2$ per one firing is suitable. The reproducibility of the measurements decreased with decreasing Pd content. The sensitivity of analyte determination in the graphite atomizer generally varies with the number of firings; rapid changes in sensitivity can occur in the first few tens of atomization cycles.[21] The above-described double peak for the graphite atomizer[20] was observed likewise for some samples of lichens and mosses. Nevertheless, this was only in the case of an insufficient amount of matrix modifier being used (a Pd content of approximately 5 μg per one firing and lower), and also for a new atomizer up to the first 20–30 firings.

On the basis of measurements of the spectral environment (Fig. 3), the commonly-used wavelengths of 287.4 nm and 294.4 nm for the determination of Ga by ETAAS appear to be unusable for the analysis of environmental samples using line-source spectrometers. A wavelength of 287.4 nm is not suitable for HR-CS AAS. The calibration line for a wavelength of 287.424 nm exhibits good linearity (Fig. 2a); however, there was direct interference from iron at a wavelength of 287.417 nm (Fig. 3a) during the analysis of environmental samples. The relative sensitivity of the Fe atomic line is relatively low;[24] however, high concentrations of Fe in the environment (rock, soil, and dust particles) significantly limit the use of the Ga atomic line at 287.424 nm for environmental analyses. In addition, background overcompensation has been reported for the determination of Ga at the 287.4 nm atomic line using a line-source spectrometer with Zeeman-effect background correction due to spectral interference with the σ-component of iron.[25] The atomic line at 294.364 nm is accompanied by another less sensitive Ga line (294.417 nm), which causes the curvature of the calibration line (Fig. 2a) already from a concentration of 25 μg L^{-1}. Therefore, it can only be used for measurements with HR-CS ETAAS, which allows for the resolution of the two lines.

Thus, the only usable Ga atomic line in ETAAS with a line radiation source is that at 417.204 nm. Moreover, the emission intensity of the hollow cathode lamp at this wavelength was high,[26] which leads to an advantageous signal-to-noise ratio. The calibration line at the 417.2 nm wavelength (0.2 nm slit) is linear up to a concentration of 100 μg L^{-1} (Fig. 2b). The LOD and LOQ were 7 and 22 μg kg^{-1}, respectively. The LOD of the developed method is higher than that of ETAAS with preconcentration techniques, but lower than that of FAAS with preconcentration.[6] The advantage of the direct determination of Ga without any preconcentration is the low relative standard deviation (RSD) of the measurement (up to 5% for standards and samples).

The accuracy of the proposed method was verified by comparing its results to those obtained using a reference method. A set of 12 real samples was analyzed, covering all the matrices used in this study. As presented in Fig. 3, the reference method (HR-CS ETAAS) does not suffer from spectral interference at

Fig. 4 Comparison of Ga concentration determined using ETAAS at 417.2 nm and 294.4 nm against a reference method.

Fig. 5 Ga contents in Antarctic terrestrial flora.

either the 294.364 or 417.204 nm spectral lines. Therefore, the results obtained using HR-CS ETAAS at both lines did not differ. As shown in Fig. 4, the proposed method provided correct results using the 417.2 nm line only. No statistical difference was observed between the reference method and the developed method. Conversely, the measurement at 294.4 nm did not yield correct results due to the aforementioned spectral interferences.

The accuracy of the method was also assessed by measuring the recovery of spiked real samples. High accuracy was achieved with a recovery of 98% and an RSD of up to 3%, suggesting minimal matrix effects and reliable quantification. The inter-day repeatability, expressed as the three-day variability of the calibration slopes, reached 5%.

Ga content in Antarctic flora. The Ga contents of the Antarctic lichen, moss, mushroom, and grass samples are presented in Fig. 5. The Ga content in the moss and grass samples varied over a relatively wide range, which may be due to the incorporation of inorganic material from the subsoil into the biological structures. Surface cleaning of the sample did not guarantee complete removal of the inorganic components in the studied material. The samples were subjected to the same analytical procedures in a clean laboratory. The lowest Ga content was observed in lichen samples.

According to our research, these data are the first Ga content determined in Antarctic flora. The history of Ga research in the biosphere is summarized by Yuan et al.[3] They determined that the contents of Ga in lichens and bryophytes can be up to 60 mg kg^{-1}. Contents of 2.3–180 mg kg^{-1} in *Parmelia sulcata* lichen in the Netherlands was determined in 1986.[16] In more recent works, Ga contents of up to 9.66 mg kg^{-1} were determined in lichens samples in the USA;[17] Ga contents in moss samples in Norway ranged from 0.14–16 mg kg^{-1}.[18] By contrast, the content of Ga in mushrooms is significantly less explored. In higher mushrooms, Ga contents of up to 0.2 mg kg^{-1} were determined in *Macrolepiota procera*,[27] and up to 1.7 mg kg^{-1} in *Leccinum scabrum*[28] in Poland. The content of Ga in both cultivated and wild mushrooms is usually up to 1 mg kg^{-1}.[29]

Based on the very low Ga content in lichens as biomonitors of atmospheric pollution, generally low long-distance anthropogenic pollution in this locality can be assumed. Thus, the Ga content determined in this study can be considered as the background for the South Shetland Islands.

CONCLUSION

An analytical method for the determination of Ga by ETAAS was proposed that uses the spectral line for Ga at a wavelength of 417.204 nm, which, to the best of our knowledge, has not previously been used in the analysis of environmental samples by ETAAS. The method has a detection limit of 7 µg kg^{-1} without any preconcentration. The linearity of the measurement is in the concentration range up to 100 µg L^{-1}. The developed method can be used to determine Ga content in the plant matrix after sample mineralization.

The Ga content of Antarctic flora was determined for the first time. The very low Ga contents found in lichens (up to 0.24 mg kg^{-1}) indicate minimal Ga contamination through atmospheric deposition.

AUTHOR INFORMATION

Ondřej Zvěřina, a Ph.D. graduate from Masaryk University in Brno, Czechia, is passionate about exploring the potential of high-resolution continuum source atomic absorption spectrometry (HR-CS AAS) for elemental analysis. His research focuses on developing methods for the assessment of potentially toxic elements in the environment, with a particular interest in the Antarctic ecosystem.

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Notes

The authors declare no competing financial interest.

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