Talanta 155 (2016) 358–362

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Analysis of high-purity germanium dioxide by ETV-ICP-AES with preliminary concentration of trace elements

Nickolay S. Medvedev [a], Anastasiya V. Shaverina [a], Alphiya R. Tsygankova [a,b], Anatoly I. Saprykin [a,b,*]

[a] Nikolaev Institute of Inorganic Chemistry, Siberian Branch of Russian Academy of Sciences (NIIC SB RAS), 3, Acad. Lavrentiev Ave. Novosibirsk 630090, Russia
[b] Novosibirsk National Research State University, 2, Pirogova St., Novosibirsk 630090, Russia

ARTICLE INFO

Article history:
Received 5 November 2015
Received in revised form
19 February 2016
Accepted 20 February 2016
Available online 23 February 2016

Keywords:
Inductively coupled plasma atomic emission spectrometry
Electrothermal vaporization
Preconcentration of impurities
High-purity germanium dioxide analysis
Limits of detection

ABSTRACT

The paper presents a combined technique of germanium dioxide analysis by inductively coupled plasma atomic emission spectrometry (ICP-AES) with preconcentration of trace elements by distilling off matrix and electrothermal (ETV) introduction of the trace elements concentrate into the ICP. Evaluation of metrological characteristics of the developed technique of high-purity germanium dioxide analysis was performed. The limits of detection (LODs) for 25 trace elements ranged from 0.05 to 20 ng/g. The accuracy of proposed technique is confirmed by “added-found” («or spiking») experiment and comparing the results of ETV-ICP-AES and ICP-AES analysis of high purity germanium dioxide samples.

1. Introduction

The high-purity germanium (purity of the material should be not less than 99,999%) has semiconductor properties and is widely used in electronics industry and solar technology [1]. High-purity germanium dioxide (GeO_2) is used as a precursor for the high purity germanium and bismuth germanate scintillation single crystals [2,3]. Also germanium dioxide is used in manufacture of optical glass and as material for optical fibers and optical waveguides. Functional properties of germanium dioxide are highly dependent upon the concentration of trace elements levels. For the analysis of germanium and germanium dioxide samples the following methods of quantitative analysis are used: atomic absorption spectrometry with electrothermal atomization (ETA-AAS), direct current arc atomic emission spectrometry (D.C. arc AES), ICP-AES, inductively coupled plasma mass spectrometry (ICP-MS) [4–13]. Ultra-pure and high-purity Ge and GeO_2 containing total amount of impurities less than 10^{-3} wt% are actual for many spheres, so that the quality control of functional materials based on this materials requires using highly sensitive, multi-element and accurate methods of chemical analysis.

The preconcentration of trace elements by distilling off a sample matrix at a sample preparation step could reduce interferences of matrix components and background level which helps to improve the limits of detection (LOD) of traces. Usually a concentrate of trace elements after distilling off matrix is a solid of ≤ 1 mg or an acid solution of ≤ 50 µl. For traditional ICP-AES analysis with standard sample introduction system into the ICP (pneumatic nebulizer) concentrates have to adjusted to 2–5 ml. The dilution of the concentrates leads to reduction of the analytical signal and thus to increase LODs. The dilution procedure requires quantities of reagents exceeding of 10^2–10^3 times the concentrate volume, which leads to a high probability of contamination by impurities of reagents.

The alternative sample introduction method is the electrothermal vaporization (ETV). ETV is used for ICP-AES and ICP-MS analysis and has high transport efficiency (25–80%) that significantly higher than the efficiency of pneumatic nebulization [14–18]. For this reason, the ETV-ICP-AES analysis requires only a few microliters of solution and there is no need dilution step for the analysis of the concentrates. Using ETV-device will decrease the coefficient of dilution samples and reduce the level of the trace elements LODs. We found the publications about using of ETV for oxide analysis (for example, titanium dioxide and niobium pentaoxide) [19,20]. There are publications which are devoted to the development of ETV-ICP-MS method with introduction of suspensions of analyzed samples without preliminary concentration

---

[*] Corresponding author at: Nikolaev Institute of Inorganic Chemistry, Siberian Branch of Russian Academy of Sciences (NIIC SB RAS), 3, Acad. Lavrentiev Ave., Novosibirsk 630090, Russia.
E-mail address: saprykin@niic.nsc.ru (A.I. Saprykin).

http://dx.doi.org/10.1016/j.talanta.2016.02.052
0039-9140/

of trace elements.

The aim of the present study was to develop the ETV-ICP-AES techniques for high-purity germanium dioxide analysis with preliminary concentration of trace elements.

2. Materials and methods

2.1. Instrumentation

The measurements were performed using an iCAP 6500 Duo ICP-AES spectrometer (Thermo Scientific, USA). The spectrometer is equipped with a solid state Charge Injection Device (CID 86 chip), which allows to record transient signals. The plasma is observed axially to obtain the best possible sensitivity. Background corrected signals were used for signal quantification.

For the sample introduction at ETV-ICP-AES analysis an ETV device (VMK-Optoelectronica, Russia) was used. The ETV device is shown in Fig. 1.

For the ETV-ICP-AES analysis 50 µl of sample or standard solution was pipetted into the graphite tube (standard pyro-coated graphite furnace for ETV-AAS instrumentations were used). To prevent loss of the analytes the injection port was closed by graphite stopper. Electric current was supplied to the holders from computer controlled power supply for heating of the graphite furnace tube. Carrier argon gas flow transported vapour of the sample into the ICP by 50 cm long and 4 mm internal diameter PTFE tube. The emission spectra were measured on the second entrance slit of the spectrometer (wavelength range 194–847 nm) and the peak areas of the transient signals of the analytes were integrated for the quantitative analysis.

For the ICP-AES analysis the standard sample introduction system of iCAP 6500 was used. It includes peristaltic pump, spray chamber and glass concentric pneumatic nebulizer. The emission spectra of the analytes were measured on both entrance slits of the spectrometer (wavelength ranges 166–234 nm, 5 s and 194–847 nm, 15 s). Optimized instrumental parameters of the iCAP 6500 Duo and ETV device used in the present study are listed in Table 1.

2.2. Reagents and materials

High-purity nitric acid (HNO_3, 12 M) and high-purity hydrochloric acid (HCl, 9 M) were additionally purified by double distillation without boiling using DuoPUR, Milestone (USA). High-purity water (18.2 MΩ) purified by Direct-Q3, Millipore (USA) system was used. For preparation of multi-elemental standard solutions MES SKAT (Russia) were used. The elements concentration in the MES SKAT solutions were: MES-1: Al, Cd, Cr, Fe, Mg, Mn, Na, Zn (50 µg/ml), K (37.5 µg/ml), P (67.4 µg/ml); MES SKAT-2: B, Co, Cu, Ga, In, Ni, Si, Ti, V (50 µg/ml) Na (81.9 µg/ml); MES-3: As, Pb, Sb, Se, Sn, Te (50 µg/ml), Ag, Ba, Be, Sr (20 µg/ml), MES-4: Hf, Mo, Nb, Re, Ta, W, Zr, (50 µg/ml). Argon 99.996 purity grade was used for ETV-ICP-AES measurements.

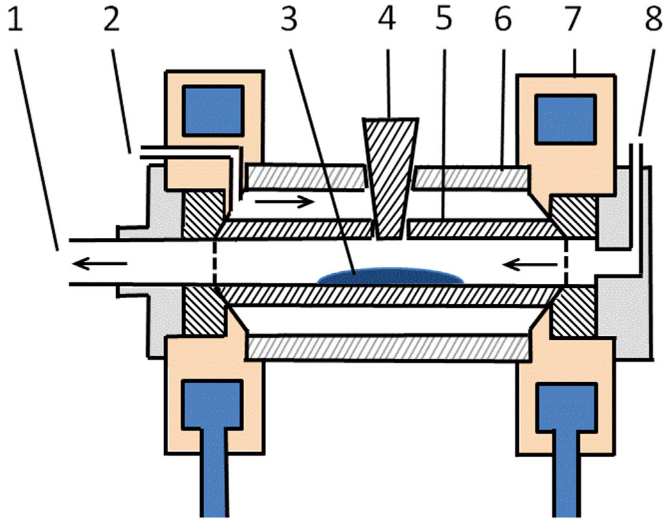

Fig. 1. ETV device (VMK-Optoelectronica): 1 – ETV-ICP transport tube, 2 – protecting gas flow (Ar), 3 – sample (concentrate), 4 – graphite stopper, 5 – graphite tube, 6 – quartz tube, 7 – water cooled holders, 8 – carrier gas flow (Ar).

Table 1
Instrumental parameters used for ETV-ICP-AES and ICP-AES analysis.

ICP parameters	
Rf power	1150 W
Auxiliary argon flow rate	0.8 l/min
Cooling argon flow rate	12 l/min
ICP viewing	Axial
ICP-AES analysis parameters	
Nebulizing argon flow rate	0.7 l/min
Flow rate of solution delivery with a peristaltic pump	0.7 ml/min
Integration time (first slit /second slit)	15/5 s
ETV-ICP-AES parameters	
Carrier argon flow rate	0.8 l/min
Protecting argon flow rate	0.6 l/min
Temperature of drying step	95 °C
Hold time of drying step	50 s
Temperature of vaporization and cleaning step	2400 °C
Hold time of vaporization and cleaning step	10 s
Integration time (second slit)	10 s

2.3. Preliminary concentration of trace elements

Following preconcentration procedure based on distilling off matrix element (Ge) was used: ∼250 mg of germanium dioxide sample were dissolved in 3 ml of HCl at 80 °C (*t*∼5–6 h). The trace elements preconcentration process carried out using PTF-bowl with conical bottom. After dissolution of germanium dioxide samples the solutions were evaporated to dry salts in the laminar flow box under infrared lamp at the temperature ∼80 °C. Then 50 µl of high-purity HNO_3 were added to the dry residue and the solution was again evaporated to dryness. For the ETV-ICP-AES analysis the dry residues were dissolved in 50 µl of 0.5 M HNO_3. For the ICP-AES analysis residues were dissolved in 50 µl of HNO_3 then diluted with high-purity water to 2 ml.

For real sample analysis the external calibration method was used. Calibration solutions were prepared from MES SKAT 1–4 solutions and 0.5 M HNO_3. In a samples preparation process plastic and PP tubes (10–15 ml) were used. The calibration functions were plotted using three points, the maximum concentration of analytes was 0.5 ppm. It was found by D.C. arc AES, after the distilling off the sample matrix the amount of germanium dioxide in the concentrate was not exceed 1% of initial weight. The experimental results have shown that the optimization of ICP-AES analysis conditions and the right choice of the analytical lines of determined elements provide absence of the matrix and spectral interferences influence.

3. Results and discussion

3.1. Optimization of ETV parameters

The temperature program of electrothermal vaporization includes three steps of graphite furnace heating: drying, vaporization and cleaning. The heating of graphite furnace at the drying