



## Technical note

# Comparison of analytical performances of inductively coupled plasma mass spectrometry and inductively coupled plasma atomic emission spectrometry for trace analysis of bismuth and bismuth oxide

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## ABSTRACT

The paper presents a comparison of analytical performances of inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma atomic emission spectrometry (ICP-AES) for trace analysis of high purity bismuth and bismuth oxide. Matrix effects in the ICP-MS and ICP-AES methods were studied as a function of Bi concentration, ICP power and nebulizer flow rate. For ICP-MS the strong dependence of the matrix effects versus the atomic mass of analytes was observed. For ICP-AES the minimal matrix effects were achieved for spectral lines of analytes with low excitation potentials. The optimum degree of sample dilution providing minimum values of the limits of detection (LODs) was chosen. Both methods let us to reach LODs from  $n \cdot 10^{-7}$  to  $n \cdot 10^{-4}$  wt% for more than 50 trace elements. For most elements the LODs of ICP-MS were lower in comparison to ICP-AES. Validation of accuracy of the developed techniques was performed by “added-found” experiments and by comparison of the results of ICP-MS and ICP-AES analysis of high-purity bismuth oxide.

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## 1. Introduction

High-purity bismuth and bismuth oxide (III) are used as precursors for a number of materials with special functional properties. Bismuth ortho-germanate ( $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ ) is a scintillator material for detectors of ionizing radiation, which are used in nuclear physics, high energy physics, tomography, etc. [1,2]. Bismuth tellurite ( $\text{Bi}_2\text{TeO}_5$ ) has non-linear optical properties. Using of bismuth tellurite for holographic materials is promising [3,4]. High purity bismuth and solid solutions on the basis of bismuth telluride ( $\text{Bi}_2\text{Te}_3$ ) have thermoelectric properties [5,6].

It is known that the functional properties of materials are greatly influenced by their main and trace composition and purity of its precursors. For example, scintillation characteristics (radiation resistance, light output, transparency, etc.) of bismuth ortho-germanate greatly depend on the content of trace elements such as Ca, Co, Cr, Eu, Fe, Mg, Mn, Ni, Pb and Yb [7–10]. Unfortunately, there is still not enough information about influence of individual trace on the functional properties of materials. In general to improve functional properties of the materials it is necessary to increase the degree of purification of precursors. This

requires developing the multielement and high-sensitivity analytical methods such as ICP-MS and ICP-AES [11].

For bismuth and bismuth oxide analysis the atomic absorption spectrometry with electrothermal atomization (ETA-AAS), atomic emission spectrometry with excitation in the dc arc (DCA-AES) and inductively coupled plasma, mass spectrometry with laser ionization (LIMS) techniques are used [12–18]. ETA-AAS has very low LODs (at ng/g level), but it is usually used for single or number elements determination. The using of DCA-AES is limited by a low number of DCA-AES spectrometers and necessity to use high purity graphite electrodes and powder. One of the most informative methods for the analysis of bismuth and bismuth oxide is LIMS. This method allows the direct analysis of bismuth oxide powder samples pressed in pellets, but nowadays the commercial LIMS spectrometers are not available. LODs of trace elements that provide an ICP-AES method often do not satisfy the requirements of modern technologies. The preliminary concentration of trace elements by distilling off the matrix at a sample preparation step could improve the LODs of analytes. But the complexity of the sample preparation step and demands of special equipment and high-purity reagents significantly complicate and increase the cost of the analysis procedure. Currently the ICP-MS is one of the most informative methods for the quantitative chemical analysis of high-purity substances. This multielement method has a very low LODs and wide dynamic range. Thus using of ICP-MS for trace analysis of high purity bismuth and bismuth

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oxide seems to be promising. But both ICP-MS and ICP-AES methods are not free from matrix effects.

The matrix effects in ICP-MS are related to spectral interferences and signal intensity changes [19–22]. In present time there are the databases of spectral interferences caused by overlap ions into most commercial ICP-MS spectrometers. The changes of signal of analyte in ICP-MS in the presence of high concentration of matrix element is due to several factors: effect on nebulizer performance and aerosol transport into ICP, ionization of the matrix element and its contribution to the electron densities in the ICP, ion transport from the ICP through the sampling interface and ion optics to the detector [23,24]. Matrix effect depends on nebulizer flow rate [22,25]. The ionization potential and the atomic mass of the analyte and matrix element are the critical factors determining the magnitude of matrix effects [22,26–28]. It was shown that for ICP-MS the heavier the atomic mass of the matrix element, the greater is the analyte signal suppression [26,28]. The goals of this work were to study the matrix effect of the ICP-MS and ICP-AES analysis of bismuth, to choose optimal instrumental parameters (ICP power, nebulizer flow rates), concentration of matrix element and to compare the analytical performances of ICP-MS and ICP-AES methods.

## 2. Materials and devices

### 2.1. Instrumentation

For ICP-MS analysis a quadrupole spectrometer iCAP Q (Thermo Fisher Scientific, USA) was used. For ICP-AES analysis the iCAP 6500 Duo (Thermo Fisher Scientific, USA) spectrometer was used. The plasma is observed axially to obtain the best possible sensitivity. Background corrected signals were used for signal quantification. The typical instrumental parameters are shown in Table 1, analytical isotopes used for ICP-MS measurements and spectral lines used for ICP-AES measurements are presented in Table 2.

### 2.2. Reagents and materials

Analyte and matrix solution were prepared using high-purity nitric acid (HNO<sub>3</sub>, 12 M) and high-purity hydrochloric acid (HCl, 9 M) obtained from sub-boiling distillation system (DuoPUR, Milestone, USA). High-purity water (18.2 MΩ) was purified by Direct-Q3, Millipore (USA) system. Solutions for quantitative measurements were prepared using standard multielement MES solutions (Skat, Russia), containing: MES 1: Al, Ca, Cd, Cr, Fe, K, Mg, Mn, Na, P, Zn (50 mg L<sup>-1</sup>), Li (10 mg L<sup>-1</sup>); MES 2: B, Bi, Co, Cu, Ga, In, Ni, Si, Ti, V (50 mg L<sup>-1</sup>); MES 3: As, Pb, Rb, Sb, Se, Sn, Te (50 mg L<sup>-1</sup>), Ba, Sr (20 mg L<sup>-1</sup>), Ag, Au, Be (10 mg L<sup>-1</sup>), Hg (5 mg L<sup>-1</sup>); MES 4: Hf, Mo, Nb, Re, Ta, W, Zr (50 mg L<sup>-1</sup>), MES REE (rare earth elements): Ce, Dy, Er, Eu, Gd, Ho, La,

**Table 1**  
Instrumental parameters of ICP-MS and ICP-AES analysis.

Parameter	ICP-MS	ICP-AES
ICP power, W	700–1600	750–1350
External argon flow rate, L min <sup>-1</sup>	14	12
Auxiliary argon flow rate, L min <sup>-1</sup>	0.8	0.5
Nebulizing argon flow rate, L min <sup>-1</sup>	0.6–1.5	0.5–1.3
Flow rate of solution delivery with a peristaltic pump, mL min <sup>-1</sup>	0.4	1.5
Integration time, s	0.1 for each mass, 10 scans	10
Pneumatic nebulizer	MicroFlow PFA-ST, Elemental Scientific	SeaSpray Nebulizer, Glass Expansion
Spray chamber	Quartz Cyclonic Spray Chamber, Thermo Scientific. Cooled to 3° C	Cyclonic Spray Chamber, Glass Expansion

**Table 2**  
Analytical isotopes and spectral lines for bismuth analysis.

Analyte	Analytical isotopes, u (ICP-MS)	Spectral lines, nm (ICP-AES)	Analyte	Analytical isotopes, u (ICP-MS)	Spectral lines, nm (ICP-AES)
Li	7	I 670.7**	Ag	107	I 338.2
Be	9	II 313.1	Cd	111	II 226.5
B	11	I 249.7	In	115	I 325.6
Na	*	I 589.6	Sn	118	II 189.9
Mg	24	II 279.5	Sb	121	I 206.8
Al	27	I 396.1	Te	125	I 214.2
Si	*	I 251.9	Cs	133	I 455.5
P	*	I 178.2	Ba	137	II 455.4
K	*	I 766.4	La	139	II 333.7
Ca	44	II 393.3	Ce	140	II 404.0
Sc	45	II 361.3	Pr	141	II 414.3
Ti	48	II 334.9	Nd	146	II 401.2
V	51	II 292.4	Sm	147	II 330.6
Cr	52	II 267.7	Eu	153	II 381.9
Mn	55	II 257.6	Gd	157	II 335.0
Fe	57	II 238.2	Tb	159	II 350.9
Co	59	II 231.6	Dy	163	II 364.5
Ni	60	II 228.6	Ho	165	II 345.6
Cu	63	II 324.7	Er	166	II 337.2
Zn	66	II 202.5	Tm	169	II 313.1
Ga	71	I 287.4	Yb	172	II 328.9
As	75	I 193.7	Lu	175	II 261.5
Se	77	I 196.0	Hf	178	II 339.9
Rb	85	I 780.0	Ta	181	II 268.5
Sr	88	II 407.7	W	182	II 207.9
Y	89	II 371.0	Re	185	II 197.3
Zr	90	II 339.1	Au	197	I 267.5
Nb	93	II 309.4	Hg	202	I 184.9
Mo	95	II 204.5	Pb	208	I 261.4

\* Spectral interferences.

\*\* I – atomic line, II – ionic line.

Lu, Nd, Pr, Sm, Tb, Tm, Sc, Y (50 mg L<sup>-1</sup>), Yb (25 mg L<sup>-1</sup>). Argon of 99.996 purity grade was used for ICP-MS and ICP-AES measurements.

The initial solution for ICP-MS analysis of the bismuth and bismuth oxide was prepared as follows. 1 mL of high-purity nitric acid was added to 100 mg of high-purity bismuth oxide sample. The sample was dissolved by heating on a water bath. After sample dissolution 0.5 mL of deionized water was added. The analyzed solutions were prepared by dilution of the initial solution by 0.5 M nitric acid to the required Bi concentration. The solutions for calibration were prepared in a same manner using high purity bismuth oxide. The analytes were introduced into the calibration solution from the MES at the stage of the initial solution dilution.

For ICP-AES analysis 670 mg of bismuth oxide were dissolved in high-purity nitric acid. After dissolution the solutions were diluted by deionized water to a Bi concentration equal 6 wt%.

## 3. Results and discussion

### 3.1. Matrix effect in ICP-MS and ICP-AES

#### 3.1.1. Matrix-induced changes in analyte signals at different Bi concentration

In order to reduce matrix effects the analyzed samples (solutions) must be significantly diluted. It is important to choose the optimal degree of dilution providing a low matrix effect. We studied the dependence of analytical signal vs matrix element (Bi) concentration in solution. For ICP-MS measurements the concentrations of analytes were 50 µg L<sup>-1</sup>, Bi concentration varied from 0.01 to 6 g L<sup>-1</sup> wt. For ICP-AES measurements the concentrations of analytes were 200 µg L<sup>-1</sup>, Bi concentration varied from 1 to 60 g L<sup>-1</sup> wt.

It has been found that the character of ICP-MS matrix effects is strongly depends on the atomic mass of analytes. Fig. 1 shows typical dependences of the analytical signal ratio I<sub>i</sub>/I<sub>0</sub> (I<sub>i</sub> is the intensity of

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