

Determination of Impurities in Bismuth Oxide by Laser Mass Spectrometry

D. Yu. Troitsky and A. I. Saprykin

*Nikolaev Institute of Inorganic Chemistry, Siberian Branch, Russian Academy of Sciences,
pr. Akademika Lavrent'eva 3, Novosibirsk, 630090 Russia
e-mail: dmitroitsk@niic.nsc.ru*

Received August 4, 2014

Abstract—We have developed a technique for the quantitative analysis of bismuth oxide by laser mass spectrometry. The technique makes it possible to determine up to 70 impurities in the range 10^{-6} to 10^{-4} wt %. To evaluate relative sensitivity factors and obtain calibration plots, we used reference samples prepared by diluting a standard SOG-21-1 graphite sample with high-purity bismuth oxide powder.

DOI: 10.1134/S0020168515060175

INTRODUCTION

High-purity bismuth oxide is used as a precursor in the preparation of ferroelectric ceramics, specialty glass, and scintillator crystals [1–3]. These application areas impose special requirements on the purity of starting materials, in combination with a necessity to develop and improve multielement approaches to the determination of impurities in bismuth oxide [4–9]. One effective multielement analytical technique is laser mass spectrometry (LMS), which makes it possible to simultaneously determine up to 70 impurity elements in solid samples, with detection limits down to 10^{-6} wt % [10]. One important advantage of this technique is that there is no need to dissolve samples to be investigated, which rules out contamination of the samples in the sample preparation process. LMS is thought to be a semiquantitative technique because, for most solid materials, including bismuth oxide, there are no certified standard samples, which makes it impossible to determine the relative sensitivity factors of impurity elements with respect to the host. The lack of certified standards leads to uncertainties in quantitative chemical analysis data.

To ensure a quantitative LMS analysis of high-purity bismuth oxide, we proposed a calibration technique with the use of reference samples prepared by diluting the State Standard Sample 4519-89/4523-89 (SOG-21-1 graphite) with high-purity bismuth oxide.

EXPERIMENTAL

In this study, we used an EMAL-2 double-focusing laser ionization mass spectrometer with Mattauch–Herzog geometry (Elektron Production Association). The light source used was a *Q*-switched Nd:YAG laser

($\lambda = 1.064 \mu\text{m}$; pulse repetition rate, 50 Hz). Mass spectra were recorded on UF-4 photographic film.

Reference samples were prepared using an SOG 21-1 graphite standard sample (State Standard Sample 4519-89/4523-89) with certified weight fractions of 21 elements at a level of 1×10^{-1} wt % and high-purity (6N) bismuth oxide (Furukawa Denshi Co). The impurity contents of the high-purity bismuth oxide sample, which was analyzed for 21 elements by LMS, are listed in Table 1. It is seen that the percentages of the impurities in this sample are below the respective detection limits.

To prepare the reference samples, 1 mg of SOG-21-1 graphite was added to 1 g of high-purity bismuth oxide (Furukawa Denshi Co) and the mixture was ground in a Plexiglas mortar for 20 min. Since the SOG 21-1 standard contained no chlorine, chlorine was added in the form of potassium chloride.

Samples for LMS analysis were prepared by pressing into pellets 10 mm in diameter. Before pressing into pellets, a sample under study (0.5 g) was placed in a die between tantalum foil inserts (TVCh high-purity tantalum, Purity Standard TU 95.311-82) 50 μm in thickness, precleaned by etching in a mixture of HNO_3 and HF (1 : 10). After pressing at $\sim 20 \times 10^5$ Pa, the pellet was withdrawn from the die, the tantalum inserts were removed, and the pellet was placed in the ion source chamber of the EMAL-2 mass spectrometer, which was then pumped down to a pressure of 1×10^{-4} Pa (2 h). After that, an accelerating voltage was applied and laser radiation was directed to the pellet surface. The surface was scanned with the laser beam over an area of $5 \times 5 \text{ mm}^2$ to remove possible surface contamination. After the laser surface processing, mass spectra were taken. An analytical signal (blackening of analytical lines of the elements to be determined) was measured using an MD-100 automated

Table 1. Estimated impurity contents of 6N bismuth oxide (Furukawa Denshi Co)

Element	wt %	Element	wt %
B	$\leq 2 \times 10^{-4}$	Mn	$\leq 1 \times 10^{-5}$
C	$\leq 5 \times 10^{-4}$	Fe	$\leq 1 \times 10^{-5}$
Na	$\leq 7 \times 10^{-6}$	Co	$\leq 1 \times 10^{-5}$
Mg	$\leq 8 \times 10^{-6}$	Ni	$\leq 2 \times 10^{-5}$
Al	$\leq 9 \times 10^{-6}$	Cu	$\leq 2 \times 10^{-5}$
Si	$\leq 1 \times 10^{-5}$	Zr	$\leq 2 \times 10^{-5}$
Cl	1×10^{-4}	Nb	$\leq 1 \times 10^{-5}$
Ca	$\leq 1 \times 10^{-5}$	Mo	$\leq 3 \times 10^{-5}$
Ti	$\leq 2 \times 10^{-5}$	Cd	$\leq 3 \times 10^{-5}$
V	$\leq 1 \times 10^{-5}$	Ta	$\leq 5 \times 10^{-5}$
Cr	$\leq 1 \times 10^{-5}$	W	$\leq 5 \times 10^{-5}$

Table 2. Results of standard addition experiments (all of the elements, except carbon, were added in a concentration of 1×10^{-3} wt %; the carbon concentration was 1×10^{-1} wt %)

Element	Found, wt % ($n = 5, P = 0.95$)	RSF
B	$(6.4 \pm 2.2) \times 10^{-5}$	0.06
C	$(1.8 \pm 0.6) \times 10^{-1}$	0.18
Na	$(7.4 \pm 1.8) \times 10^{-4}$	0.7
Mg	$(7.0 \pm 2.5) \times 10^{-4}$	0.7
Al	$(6.6 \pm 2.1) \times 10^{-4}$	0.7
Si	$(7.0 \pm 1.7) \times 10^{-4}$	0.7
Cl	$(7.8 \pm 2.2) \times 10^{-4}$	0.8
Ca	$(7.8 \pm 2.2) \times 10^{-4}$	0.8
Ti	$(0.9 \pm 0.4) \times 10^{-4}$	0.9
V	$(8.0 \pm 2.8) \times 10^{-4}$	0.8
Cr	$(8.8 \pm 2.5) \times 10^{-4}$	0.9
Mn	$(8.2 \pm 2.7) \times 10^{-4}$	0.8
Fe	$(7.8 \pm 2.2) \times 10^{-4}$	0.8
Co	$(1.0 \pm 0.3) \times 10^{-3}$	1.0
Ni	$(1.0 \pm 1.7) \times 10^{-4}$	1.0
Cu	$(1.1 \pm 0.4) \times 10^{-3}$	1.1
Zr	$(1.2 \pm 0.4) \times 10^{-3}$	1.2
Nb	$(1.2 \pm 0.4) \times 10^{-3}$	1.2
Mo	$(1.1 \pm 0.5) \times 10^{-3}$	1.1
Cd	$(1.4 \pm 0.5) \times 10^{-3}$	1.4
Ta	$(1.6 \pm 0.5) \times 10^{-3}$	1.6
W	$(1.8 \pm 0.6) \times 10^{-3}$	1.8

microphotometer. To convert the blackening of the lines to intensities, which are proportional to element concentrations, we used a characteristic emulsion curve of the photographic plate, which was preplotted using ten tin isotopes (with natural abundances) recorded on the photographic plate.

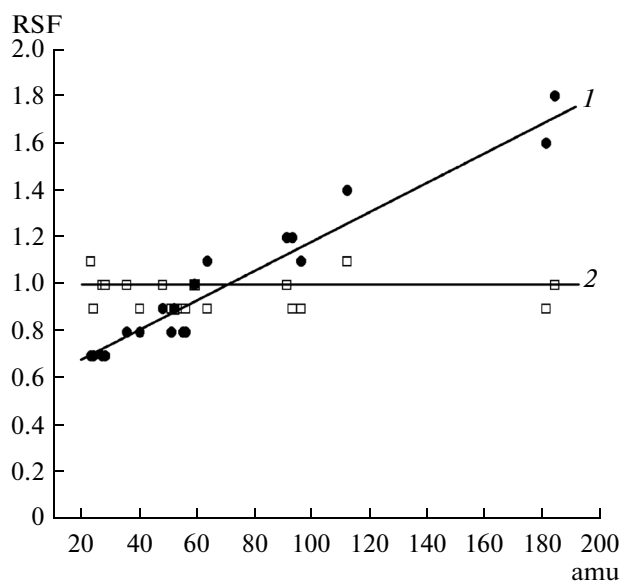
RESULTS AND DISCUSSION

Preliminary measurement results allowed us to adequately carry out standard addition experiments using a laboratory-made reference sample prepared by diluting the SOG 21-1 graphite standard sample with 6N bismuth oxide (Furukawa). As a result of dilution, the reference sample contained B, Na, Mg, Al, Si, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zr, Nb, Mo, Cd, Ta, W, and Cl impurities at a level of 1×10^{-3} wt % and 1.0 wt % carbon. The percentage of chlorine, added to the sample in the form of potassium chloride solution, was determined by atomic absorption spectroscopy and capillary electrophoresis [11], and the percentage of carbon was determined using CHN analysis. Table 2 presents the results of our standard addition experiments. For all of the elements in question, 95% confidence intervals are indicated. The experimental data were used to assess the relevant relative sensitivity factors (RSFs):

$$RSF_i = C_{i, \text{found}} / C_{i, \text{added}} \quad (1)$$

where $C_{i, \text{added}}$ is the percentage of the i th element added and $C_{i, \text{found}}$ is that evaluated from the relevant LMS data.

The RSFs for 21 impurity elements are listed in Table 2. The plot representing the data in Table 2 (figure) demonstrates that the RSF_i values increase with increasing atomic weight and range from 0.7 to 1.8. This allowed us to introduce a correction ($K_{m, i}$) taking



Relative sensitivity factor as a function of the mass of the analytical isotope of the element to be determined: (1) from the data in Table 2, (2) with the $K_{m,i}$ correction.

into account the effect of the mass number of ions on their RSFs:

$$K_{m,i} = \text{RSF} \frac{7.8}{\sqrt{m_i}}, \quad (2)$$

where m_i is the mass of the analytical isotope of the element to be determined (amu).

The correction for the mass ($K_{m,i}$) makes it possible to obtain $\text{RSF}_i = 1$ for all of the analytes (line 2) except boron and carbon, which seems to be attributable to the effect of scattered magnetic field on light element ions [12].

Using the above corrections and the $3s_f$ criterion, we evaluated the detection limits for the 70 elements that can be determined by LMS (Table 3). For most of the analytes, the detection limit lies in the range 10^{-6} to 10^{-5} wt %. The exceptions are Be, B, C, N, F, Hg, and Tl, which have higher detection limits because of the increased background produced on photographic film by strong lines of the host elements (Bi and O). Note one important advantage of LMS: the possibility of determining gas-forming elements (C and N) and halogens.

The accuracy of the procedure proposed for LMS analysis was checked by comparing analytical data obtained for a bismuth oxide sample by independent techniques: dc arc atomic emission spectroscopy (AES) and inductively coupled plasma atomic emission spectroscopy (ICP AES) [8, 9] (Table 4). The data thus obtained agree well, demonstrating adequacy of the proposed technique.

Table 3. Detection limits (C_{\min}) of LMS for impurities in bismuth oxide (evaluated using the $3s_f$ criterion)

Element	C_{\min} , wt %	Element	C_{\min} , wt %
Be	2×10^{-4}	Ru	2×10^{-5}
B	2×10^{-4}	Rh	1×10^{-5}
C	5×10^{-4}	Pd	2×10^{-5}
N	5×10^{-4}	Ag	2×10^{-5}
F	2×10^{-4}	Cd	3×10^{-5}
Na	7×10^{-6}	In	1×10^{-5}
Mg	8×10^{-6}	Sn	2×10^{-5}
Al	9×10^{-6}	Te	2×10^{-5}
Si	8×10^{-6}	I	2×10^{-5}
P	1×10^{-5}	Cs	2×10^{-5}
S	5×10^{-5}	Ba	3×10^{-5}
Cl	1×10^{-5}	La	2×10^{-5}
K	1×10^{-5}	Ce	2×10^{-5}
Ca	1×10^{-5}	Pr	2×10^{-5}
Sc	5×10^{-5}	Nd	3×10^{-5}
Ti	2×10^{-5}	Sm	3×10^{-5}
V	1×10^{-5}	Eu	2×10^{-5}
Cr	1×10^{-5}	Gd	3×10^{-5}
Mn	1×10^{-5}	Tb	2×10^{-5}
Fe	1×10^{-5}	Dy	3×10^{-5}
Ni	2×10^{-5}	Ho	2×10^{-5}
Co	1×10^{-5}	Er	3×10^{-5}
Cu	2×10^{-5}	Tm	2×10^{-5}
Zn	2×10^{-5}	Yb	3×10^{-5}
Ga	1×10^{-5}	Lu	2×10^{-5}
Ge	2×10^{-5}	Hf	4×10^{-5}
As	9×10^{-6}	Ta	5×10^{-5}
Se	1×10^{-5}	W	5×10^{-5}
Br	2×10^{-5}	Re	4×10^{-5}
Rb	1×10^{-5}	Os	5×10^{-5}
Sr	1×10^{-5}	Ir	5×10^{-5}
Y	1×10^{-5}	Pt	5×10^{-5}
Zr	1×10^{-5}	Au	4×10^{-5}
Nb	1×10^{-5}	Hg	5×10^{-4}
Mo	2×10^{-5}	Tl	8×10^{-4}

Table 4. Comparison of analytical data obtained for a bismuth oxide sample by independent techniques (wt %)

Element	DC arc AES	ICP AES	LMS
Mg	1×10^{-3}	–	$(7 \pm 3) \times 10^{-4}$
Al	7×10^{-4}	ND (5×10^{-4})	$(5 \pm 3) \times 10^{-4}$
Si*	$\leq 2 \times 10^{-3}$	$\leq 3 \times 10^{-2}$	$(4 \pm 2) \times 10^{-3}$
Ti	ND (5×10^{-4})	9×10^{-4}	$(6 \pm 2) \times 10^{-4}$
Cr	6×10^{-4}	–	$(4 \pm 2) \times 10^{-4}$
Mn	1×10^{-3}	1×10^{-3}	$(9 \pm 3) \times 10^{-4}$
Fe	1×10^{-3}	1×10^{-3}	$(1.0 \pm 0.3) \times 10^{-3}$
Ni	1×10^{-3}	4×10^{-3}	$(8 \pm 3) \times 10^{-4}$
Co	2×10^{-3}	1×10^{-3}	$(1.0 \pm 0.4) \times 10^{-3}$
Cu	3×10^{-4}	1×10^{-3}	$(3 \pm 1) \times 10^{-4}$
Zn	3×10^{-3}	2×10^{-3}	$(2.0 \pm 0.5) \times 10^{-3}$
Ge	–	–	$(1.0 \pm 0.3) \times 10^{-3}$
Y	–	–	$(8 \pm 3) \times 10^{-4}$
Pd	8×10^{-4}	–	$(1.0 \pm 0.3) \times 10^{-3}$
Ag	2×10^{-3}	ND (3×10^{-3})	$(2.0 \pm 0.5) \times 10^{-3}$
In	–	–	$(9 \pm 3) \times 10^{-4}$
Sn	–	–	$(2.0 \pm 0.5) \times 10^{-4}$
Sb	2×10^{-3}	–	$(1.0 \pm 0.5) \times 10^{-3}$
Ce	–	–	$(2.0 \pm 0.5) \times 10^{-3}$
Gd	–	–	$(3 \pm 1) \times 10^{-3}$
Er	–	–	$(2 \pm 0.5) \times 10^{-3}$
Yb	–	–	$(1.0 \pm 0.4) \times 10^{-3}$
W	–	1×10^{-2}	$(6 \pm 3) \times 10^{-3}$

* Determination is limited to the level of a control experiment. ND = Not determined.

CONCLUSIONS

We have developed a procedure for the quantitative determination of impurities in high-purity bismuth oxide by laser mass spectrometry and proposed a calibration technique for the quantitative determination of impurities in bismuth oxide using a reference sample prepared by diluting an SOG-21-1 standard sample with high-purity bismuth oxide. The technique makes it possible to determine up to 70 impurity elements with detection limits in the range 10^{-6} to 10^{-4} wt %.

Its adequacy has been demonstrated by comparing data obtained by independent techniques.

REFERENCES

1. Nath, A.K. and Medhi, N., Piezoelectric properties of environmental friendly bismuth doped barium titanate ceramics, *Mater. Lett.*, 2012, vol. 73, pp. 75–77.
2. Watanabe, T., et al., Hardness and elastic properties of Bi_2O_3 -based glasses, *J. Mater. Sci.*, 2001, vol. 36, pp. 2427–2433.

3. Novoselov, I.I., Makarov, I.V., Fedotov, V.A., Ivannikova, N.V., and Shubin, Yu.V., Synthesis of a bismuth germanium oxide source material for $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ crystal growth, *Inorg. Mater.*, 2013, vol. 49, no. 4, pp. 412–415.
4. Yukhin, Yu.M., Mikhailov, Yu.I., Afonina, L.I., and Podkopaev, O.I., Synthesis of high-purity bismuth oxide, *Vysokochist. Veshchestva*, 1996, no. 4, pp. 62–71.
5. Novoselov, I.I., Petrova, N.I., Troitskii, D.Yu., and Tkachev, D.S., Bismuth refining by vacuum distillation, *Khim. Khim. Tekhnol.*, 2006, no. 8, pp. 40–44.
6. Shelpakova, I.R., Chanysheva, T.A., Tsygankova, A.R., Rodionov, S.G., Troitskii, D.Yu., Petrova, N.I., and Saprykin, A.I., Atomic-emission spectral analysis of bismuth oxide with impurity preconcentration by reactive vaporization of the host, *Zavod. Lab. Diagn. Mater.*, 2007, vol. 73, no. 8, pp. 15–20.
7. Shelpakova, I.R., Tsygankova, A.R., and Saprykin, A.I., Determination of impurities in bismuth and its compounds (review), *Metody Ob'ekty Khim. Anal.*, 2007, vol. 2, no. 2, pp. 117–129.
8. Tsygankova, A.R., Makashova, G.V., Shelpakova, I.R., and Saprykin, A.I., Analysis of bismuth oxide by inductively coupled plasma atomic emission spectroscopy, *Zavod. Lab., Diagn. Mater.*, 2013, vol. 79, no. 3, pp. 12–16.
9. Chanysheva, T.A. and Shelpakova, I.R., Unified atomic emission analysis of various systems, *Anal. Kontrol'*, 2008, vol. 6, no. 3, pp. 298–306.
10. Sysoev, A.A., Mass spectrometric elemental analysis of solid substances in Russia, *J. Anal. Chem.*, 2011, vol. 66, no. 11, pp. 1079–1089.
11. Polyakova, E.V., Shuvaeva, O.V., and Saprykin, A.I., Chlorine impurity content of Bi_2O_3 and GeO_2 , *Inorg. Mater.*, 2008, vol. 44, no. 9, pp. 986–989.
12. Sysoev, V.I., Troitskii, D.Yu., and Saprykin, A.I., Analysis of silicon carbonitride films by laser mass spectrometry, *Mass-Spektrometriya*, 2013, vol. 10, no. 2, pp. 103–108.

Translated by O. Tsarev