Determination of B_2O_3 in Boron Nitride by Volumetric Titration

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Abstract. In this paper, researchers establish and verify a method on the determination of B_2O_3 in boron nitride through volumetric titration. Three criteria including proportionable system error, extra system error and statistics error are investigated in detail. The results show that, this method meets the requirements of chemical analytical methods with the proportionable system error of 0.35%, extra system error of 0.39% and statistics error of 0.21%. Then researchers use this method to detect samples of boron nitride. The relative standard deviation and relative accuracy are 0.27% and 0.28% respectively, which comply with the limits of acid-base titration. Therefore, the determination of B_2O_3 in boron nitride by volumetric titration method is feasible.

1. Introduction

Boron nitride material has excellent mechanical and physical properties, as well as low coefficient of thermal expansion and high thermal conductivity [1-3]; it also has advantages of high stability, high thermal conductivity, high hardness [4, 5] and broad-band gap. Ceramic materials made by boron nitride have high temperature resistance, wear resistance, corrosion resistance and other special performances. Thus, it has broad application prospects in semiconductor devices with high temperature and great powers, and in the research and development of windows with high stability and transparency [6-8]. Boron nitride ceramics also have low dielectric constant and good mechanical properties. They are widely used in aeronautics and astronautics. Thermal reaction method is the common way to produce boron nitride in the industry. Borax and boric acid are used as raw material; they are heated and refined with nitrogen compounds. In this process, unreacted boric acid produces B_2O_3. If B_2O_3 elements are left in products, they will not only affect the physical properties of ceramics, but also directly affect the nucleation of boron nitride. It can increase porosity and permanently expand the boron nitride ceramics. In tissues near the surface of materials, large number of crack sources will reduce the material strength. According to different uses of materials, it is stipulated in China that the proportion of boron oxide should be lower than 1% in first grade boron nitride, lower than 0.3% in second grade boron nitride [9]. Therefore, it is very important to accurately measure the content of boron oxide in production process.

At present, there is no national standard on analysis methods of boron oxide in boron nitride. JB/T 7994-2012, the Provision on Boron Nitride Chemical Analysis Methods does not involve boron oxide; methods of boron oxide determination in boron carbide are usually used as reference. [10] In order to guarantee accurate and reliable test results, the applicability, accuracy and scientificity of a non-standard method must be verified to prove that it can meet the requirements and objectives of the project. [11, 12]

The method for determining boron oxide in boron nitride is volumetric titration. The principle is that boron nitride is insoluble in water, while boric acid can be dissolved in hot water. Usually, researchers should test the detection limit, precision, recovery rate, linear range and other characteristics of sample matrix to verify the detection method. [13] However, volumetric titration method is different from other instrumental methods; there's no need to work out working curve during measurement. So the common concern on that method is its repeatability and accuracy of measurement, [14-16] which are obviously not enough. In European Directorate for the Quality of Medicines & Health Care Technical Guide for the Elaboration of Monographs [17], there's clear description on the technical requirements of volumetric titration method: when establishing a new

analysis method, at least 7 samples with different weights should be titrated; data ought to be analyzed statistically, and meet the requirements of "proportionable system error", "extra system error" and "statistical error" as well as other evaluation indexes. Then the new titration method can be verified. These three criteria are established on the basis of working curve; tests results are evaluated from the perspectives of linear range, system error and precision.

In this paper, the EU boron nitride standard substance ERM ED103 is used to verify the method of measuring boron oxide by volumetric titration. The accurate and reliable method for the determination of boron oxide in boron nitride powder is established.

2. Experiment

2.1 Instruments and reagents

Burette: 10mL, A level;

Magnetic stirrer: ZNCL-DL, made by Shanghai Yuezhong Instrument Equipment Co. ltd.;

Boron nitride standard material: ERM ED103, Germany BAM;

Standard sodium hydroxide solution: 0.0102 mol • L-1;

Phenolphthalein indicator (1% ethanol solution): 1g phenolphthalein indicator is dissolved in 80 mL ethanol; dilute with water to 100 mL;

Mannitol: analytical pure.

2.2 Experiment methods

1 g sample is put in 250 mL beaker; then add 70℃ hot water 80 mL; put the beaker on a magnetic stirrer, heat to 70 ℃ and maintain the temperature for 40 minutes; filter the solution when it is still hot; wash the beaker and precipitation with hot water for several times; the filtrate and washing liquid are collected in 500 mL conical flask, cooling. Add 2 g mannitol, 10 drops of phenolphthalein in above solution; add 0.1 mol L-1 standard sodium hydroxide solution, then the solution become reddish; add 2 g mannitol, if the red color disappears, continue to add standard sodium hydroxide solution, until the red color stays after adding mannitol. The titration results are corrected by blank experiment. The percentage of boron oxide is calculated according to formula (1):

$$B_2O_3(\%) = \frac{C(V - V_0) \times 34.81}{m \times 1000} \times 100 \quad (1)$$

In the formula, C stands for concentration of standard sodium hydroxide solution, mol • L^{-1}; V means the volume of consumed standard sodium hydroxide solution by samples, mL; V_0 means the volume of consumed standard sodium hydroxide solution in blank experiment, mL; *m is* the quality of sample, g

2.3 Validation method and steps

When using a new analysis method for determination, it is recommended that under prescribed conditions, random samples with different weights should be tested by titration method; the volume of consumed titration liquid at the end point of titration should be 20%~90% of the burette. Then data should be analyzed statistically, and meet a number of evaluation requirements in order to obtain recognition. Take 7 samples with different weights; experiments are performed according to procedure described in 1.2; record the consumption volume at the end point of titration; through linear regression equation, the quality of sample m and titration volume at the end point V are statistically analyzed to get gradient $b_{obs,}$ intercept a_{obs} and statistical error represented by $sdv(V)$. Then verify the results according to three criteria:

(1) Proportionable system error. Considering the titer of standard titration solution, for titration indicator method, the relative deviation between the gradient b_{obs} and theoretical value b_{theor} should not exceed 0.5%. Calculation can be seen in formulas (2) and (3).

$$\text{Proportionable system error}(\%) = \left| \frac{b_{obs} - b_{theor}}{b_{theor}} \right| \times 100 \quad (2)$$

$$b_{theor} = \frac{Z}{M_r \times C_r} \quad (3)$$

In above formulas, b_{obs} is the gradient of linear equation; b_{theor} is the titration constant; M_r is the relative molecular weight; Z is the stoichiometric coefficient of chemical reaction; Cr is the molar concentration of the titrant.

(2) Extra system error. For indicator methods, the intercept a_{obs} got through extrapolation should not exceed 0.6% of the expected or target titration volume. Calculation can be seen in formulas (4) and (5).

$$\text{Extra system error (\%)} = \frac{a_{obs}}{V_T} \times 100 \tag{4}$$

$$V_T = b_{theor} \times m \tag{5}$$

In above formulas, a_{obs} is the intercept of linear equation; V_T is the expected or target titration volume.

(3) Statistical error. For indicator methods, the estimated value of standard deviation $sdv(V)$ should not exceed 0.5% of the target or expected titration volume. Calculation can be seen in formulas (6) and (7).

$$\text{Statistical error (\%)} = \frac{sdv(V)}{V_T} \times 100 \tag{6}$$

$$sdv(V) = \sqrt{\frac{\sum_{i=1}^{n} (V_i - a_{obs} - b_{obs} m_i)^2}{n-2}} \tag{7}$$

In the formula, $sdv(V)$ is the standard deviation; Vi means volumic number of titration liquid for the ith consumption; m_i is quality of the sample; n stands for titration times.

3. Results and Discussion

Proportionable system error. Weigh 7 samples between 1 g~4.5 g, ensure consumption volume of titrant at the end point accounts for 20%~90% of the 10 mL burette. Take the sample mass as abscissa, the titration volume as ordinate, and draw the standard curve in Figure 1. The linear equation is y=1.9783x+0.0077, b_{obs}=1.9783, a_{obs} =0.0077. As the standard value of boron oxide in the standard material ERM ED103 is 0.070%, it is calculated according to formulas (2) and (3):

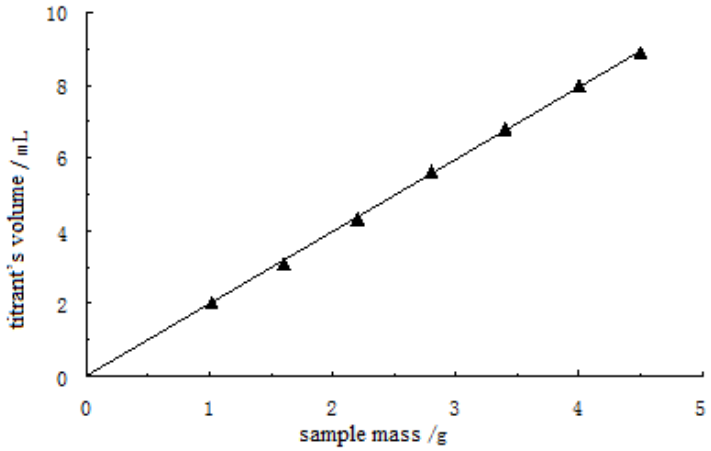

Figure 1 Linear Regression Figure

The standard deviation between the measured value and the theoretical value is $\left|\frac{1.9783-1.9715}{1.9715}\right| \times 100 = 0.35\% < 0.5\%$, which can meet the requirement of the first criteria. That is, the relative deviation between the measured value and the theoretical value should be no more than 0.5%. The results show that when the boron oxide is measured by this method, the target titration volume has a good linear relationship within 10mL.

Extra system error. According to the linear regression equation, a_{obs} =0.0077. According to formulas (4) and (5), it can be calculated that $V_T = 1.9715 \times 1 = 1.9715$. Extra system error is

$\frac{0.0077}{1.9715} \times 100 = 0.39\% < 0.6\%$. So the method is consistent with the second criterion of not exceeding 0.6% of the expected or target titration volume. The results show that the minimum error between the measured value and the actual value, namely the systematic error of that method is very small, and can be ignored.

Statistical error. According to formula (6), (7), *sdv*(*V*)=0.00416; the statistical error is

$$\frac{0.00416}{1.9715} \times 100 = 0.21\% < 0.5\%$$

The results show that, the proposed method meets the requirement of the third criteria, i.e., the estimated standard deviation *sdv*(*V*) is less than 0.5% of the expected or target titration volume V_T; the precision degree is good

The results can be seen in Table 1.

Table 1 The Statistical Results of Three Criteria

Criteria	calculated value			limitation/ %
1	b_{obs}	b_{theor}	proportionable system error /%	
	1.9783	1.9715	0.35	0.5
2	a_{obs}	V_T	Extra system error /%	
	-0.0077	1.9715	0.39	0.6
3	*sdv*(*V*)	V_T	statistical error /%	
	0.00416	1.9715	0.21	0.5

Repeatability And Accuracy. Repeatability is usually reflected by RSD, the relative standard deviation of multiple parallel values measured at the same time. Repeatability standard deviation changes with concentration. If Cs stands mass fraction of analyte in samples, the value of acceptable repeatability standard deviation RSDr can be calculated through formula (8): [11]

$$RSD_r = C_s^{-0.15} \tag{8}$$

Relative accuracy can be calculated by formula (9):

$$\Delta x = \frac{\bar{x} - \bar{x}_{theor}}{\bar{x}_{theor}} \times 100\% \tag{9}$$

When the titration method is well studied, there are enough reasons to confirm that its repeatability and accuracy do not exceed the limit values listed in table 2. [17]

Table 2 Content Analysis and Limitation

Type	content limitation /%	repeatability /%	relative accuracy /%
acid base titration	±1.0	0.33	±0.67
nonaqueous titration	±1.0	0.33	±0.67
conjugate acid	±1.0	0.33	±0.67
oxidation-reduction titration	±1.5	0.5	±1.0
argentometry	±1.5	0.5	±1.0
complexometry	±2.0	0.67	±1.33

7 samples of boron nitride are taken; each sample weighs 1 g (accurate to 0.1 mg). Parallel measurement is performed according to procedure in 1.2, and the results are shown in table 3. Table 3 shows the average measured value is 1.058%, the relative accuracy is 0.28%; the relative standard deviation is 0.27%, while the acceptable limit value of RSDr is 1%. Thus, this method has good repeatability and accuracy.

Table 3 Repeatability and Accuracy Tests

measured value /%	average value /%	standard value /%	RSD/%	Δ x/%
1.059,1.060,1.057,1.055, 1.056,1.054,1.062	1.058	1.061±0.016	0.27	0.28

4. Conclusions

Volumetric titration is the best choice in measurement of boron oxide in boron nitride. The establishment and verification of volumetric titration method should be scientific and reasonable. Through several tests on the linear range, system error, precision, repeatability, accuracy and other aspects of volumetric titration method, it is showed that this method is feasible. The results are objective and scientific; the method has good repeatability and high accuracy; it can be used in the measurement of B_2O_3 in nitrogen oxide.

References

[1] H.Z. Le, G.S. Tian, J. Ji, et al., Research on production process and characteristics of hexagonal BN powder through vacuum nitriding furnace, J. Bulletin of The Chinese Ceramic Society. 29 (2010) 444-449.

[2]Y.H. Du, G.Z. Zhang, T.C. Zhang, Study on the characteristics of ball milling six angle BN, J. Journal of Synthetic Crystal. 40 (2011) 1451-1454.

[3] T. Jiang, Z.H. Jin, G.J. Qiao, Preparation and properties of machinable B4C/BN multiphase ceramics, J. Rare Metal Materials and Engineering. 36 (2007) 585-588.

[4] S.H. Zhang, Electronic structure and thermodynamic properties of cBN, J. Journal of Chongqing Technology and Business University. 28 (2011) 301-304.

[5] S.R. Xiao, X.C. Deng, Current situation and development trend of cutting tool coating materials, J. Mineral and Processing Equipment. 27 (2006) 4-6.

[6] G.Z. Wang, Comprehensive Analyses on characteristics of cBN, J. Superhard Material Engineering.17 (2005) 41-45.

[7] X.L. Li, X.J. Wu, Low dimensional BN materials, J. Journal of University of Science and Technology of China. 22 (2014) 389-402.

[8] Y. Chen, J. Zou, Boron nitride nanotubes, J. Applied Physics Letters. 84(2004) 2430-2432.

[9] X.J. Zheng, Boron Carbon and Boron Nitrogen Compounds, Chemical Industry Press, Beijing, 2014.

[10] JB/T 7993-2012 Boron Carbide Chemical Analysis Method.

[11] General Administration of Quality Supervision, Inspection and Quarantine of PRC, Validation Procedures for Chemical Analysis Methods.

[12] Certification and Accreditation Administration of PRC, Accreditation Standards for Inspection and Testing Institutions' Qualification.

[13] CNAS 2012 CL10: The Application of Laboratory Testing and Calibration Criteria in Chemical Detections.

[14] W.E. Wu, G.W. Mao, J. Lu, Determination of total boron content in the combustion residue of boron containing fuel rich propellant by titration method, J. Physical Testing and Chemical Analysis Part B (Chemical Analysis). 44 (2008) 369-371.

[15] J.O. Zhai, Professionals, redox titration determination of chromium in Al Cr alloy, J. Physical Testing and Chemical Analysis Part B (Chemical Analysis). 43 (2007) 877-879.

[16] Wang Na, Teng Xinhua, Wang Liqiang, et al. Determination of silicon dioxide in lead zinc ore by acid soluble--potassium fluosilicate titration method, J. Metallurgical Analysis. 35 (2015) 65-69.

[17] European Directorate for the Quality of Medicines & Health Care Technical Guide for the Elaboration of Monographs. Council of Europe, France, 2005.