New sample preparation method for WD-XRF analysis of sulfide ores by fusion techniques: BN crucible for protection against contamination and quantitative retention of sulfur

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In this article, a methodology is described for the wavelength-dispersive X-ray florescence analysis of sulfide ores by fusion techniques. A boron nitride crucible is successfully utilised during pre-oxidation with no adhesion of sample powder and contamination. The combination of oxidant $LiNO_3$ and flux $Li_2B_4O_7$ at a mass ratio of 20:80 is demonstrated to be suitable for the quantitative retention of sulfur and the formation of homogeneous sample beads. The optical oxidation parameters, obtained by an orthogonal experiment $L_9(3^4)$ using the results obtained from the sulfur retention ratio using the sulfur analyser, for the quantitative retention of sulfur are as follows: temperature, 650 °C; time, 30 min and dilution ratio, 1:30. Fusion at 1000 °C indicates that sulfur does not volatilise as Li_2SO_4. The quantitative retention of sulfur in the entire process is validated by independent methods, such as X-ray diffraction, thermogravimetry–differential thermal analysis, as well as by the use of a sulfur analyser and analysis of reference materials. Moreover, 13 major elements present in sulfide ores were simultaneously and rapidly measured with precision and safety.

Introduction

Sulfide is an extremely important mineral and is the main source of several important metals; it has considerable industrial significance and economic value because of its large ore deposits. As a result, the determination of the element content in sulfide has been extensively investigated.[1] X-ray fluorescence (XRF) is the most common technique employed for the measurement of the composition of the major and trace elements present in the entire sulfide sample. However, this fusion technique has two inherent problems, which makes analysis difficult. First, the platinum–gold crucible that is typically used for the preparation of fused glasses undergoes contamination, caused by the reaction between reduced sulfur and platinum. Second, by oxygenation, sulfur is lost by volatilisation, which renders difficulty in the quantitative analysis of the sulfur concentration.

On the other hand, sulfide has long been an analytical problem in the field of XRF, and researchers have continuously investigated a solution to this problem. Baker[2] has tested various fluxes and provided three flux mixtures, which are suitable for the retention of sulfur. Norrish[3] has reported the peroxidation concept for the first time, involving the mixing of sulfide, oxidants, and flux, followed by firing the mixture in a muffle furnace at low temperature to avoid the contamination of the crucible. Guohui[4] has attempted to use a graphite crucible instead of a platinum crucible to perform peroxidation. In the following years, Spangenberg[5], Sear[6], Yao[7], Liping[8], Norman[9], Mengqi[10], Xiaoli[11], and Lihua[12] have independently attempted to optimise the oxidation processing conditions, such as type of oxidant, stabilising agent, flux and time and temperature. Recently, Gazulla[13] has demonstrated the retention of sulfur by the addition of barium in the sample to form stable $BaSO_4$. Jianbo[14] has first used agarose gel for sample preparation. Qiong[15] has proposed the use of wet chemical oxidation treatment, which involves the use of H_2O_2 to oxidise the reduced sulfur. Mingxing[16] has reported the addition of variable amounts of a stabiliser such as SiO_2, followed by oxidation, to prepare glass discs for analysis.

From the abovementioned studies, notably, contamination does not occur as long as there is no contact between the sulfide ore and crucible. Although a graphite crucible can solve this problem, it can undergo oxidation and decomposition at 600 °C in air. Moreover, the binder present in it can result in sample contamination. In recent years, a boron nitride (BN) crucible has been used for analysis.[17-19] It is advantageous as it maintains stability at 900 °C in air. Furthermore, its constituent elements are B and N; hence, it can be used for analysis as it is devoid of any sulfide. Nevertheless, until recently, there is some lack of knowledge about its use for the preparation of samples for XRF analysis. On the other hand, techniques utilising barium, agarose gel, and H_2O_2 are a little more complex than the fusion technique, and the experimental parameters are also difficult to control. Moreover, variable amounts of the added SiO_2 stabiliser can result in an inaccurate determination of SiO_2 concentration. Although Baker[2] has reported that a flux mixture of $LiNO_3$:$Li_2B_4O_7$ =

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20:80 can quantitatively retain sulfur, no pre-fire stage has been employed. Hence, contamination is not avoided, and the optimum oxidation conditions are also unknown.

In this paper, a new technique for the preparation of beads for the quantitative analysis of sulfides is developed: during oxidation, the BN crucible is employed instead of the platinum–gold crucible to prevent contamination. In addition, a sulfur analyser was employed to test the powder mixture after oxidation, as well as the sample beads, to determine the experimental parameters that guarantee the retention of sulfur by sample treatment. The result was validated by X-ray diffraction (XRD), thermogravimetry–differential thermal analysis (TG-DTA) as well as the use of reference materials.

Experimental

Materials

General reagents. The sample was oxidised using analytical-grade $LiNO_3$ obtained from Sinopharm Chemical and melted with $Li_2B_4O_7$ obtained from Claisse. Based on literature analysis, the mass ratio of $LiNO_3$ and $Li_2B_4O_7$ is maintained at 20:80 throughout the experiment. A 30 g/L NH_4Br solution, obtained from Sinopharm Chemical, was used as the bead-releasing agent.

Reference materials and samples for analysis. The following reference materials were used for calibration in wavelength-dispersive XRF (WD-XRF) analysis: GBW07162, 164 and 165 (GSO-1, 3 and 4) from the Institute of Geophysical and Geochemical Exploration, GBW07233-237 from Wuhan Institute of Geological Experiment Centre, CAN SU-1B from Natural Resources Canada and JZN-1 from the Geological Survey of Japan.

The following materials were used to validate the measurements: certified reference material CAN RTS-3A from Natural Resources Canada and GBW07163 (GSO-2) from the Institute of Geophysical and Geochemical Exploration.

Two sulfur compounds were also analysed, S12-5 and L082-3, which were collected from Yunnan Province of China.

Equipment. A custom-made BN crucible was obtained from Beijing Hong Run He, Science and Technology Co., LTD. Figure 1a shows the dimensions of the crucible.

Pre-oxidation was performed in a 4 L muffle furnace.

The beads for WD-XRF analysis were prepared using a Shimadzu Model TR Auto-Bead-1000-S apparatus.

Phase analysis was performed by XRD using a PANalytical Model X'Pert PRO XRD system with a Cu target tube and an X'Celerator detector.

Thermal analysis was performed on a TA Model SDT-Q600 simultaneous thermal analyser, which could simultaneously conduct DTA and TG analysis.

WD-XRF analysis was conducted on a PANalytical Model Axios WD-XRF spectrometer with a Rh target tube.

The sulfur content in the powder mixture after oxidation as well as in the sample beads were analysed using a LECO Model CS-844 infrared carbon sulfur analyser.

Procedure. First, sample powder with a size less than 200 meshes and oxidant $LiNO_3$ were added in the oven. Second, after drying at 105 °C for 2 h, they were stored in a desiccator to cool to room temperature.

Third, 0.2000 ± 0.0005 g of sample powder and a required amount of $LiNO_3$ were weighed and added to an agate mortar. Then, they were ground together to obtain a homogeneous mixture. Subsequently, $Li_2B_4O_7$ flux was added into the afore-mentioned mixture, followed by grinding, to obtain the final mixture. TA was performed to confirm the effect of this flux combination and choose a suitable temperature range for oxidation.

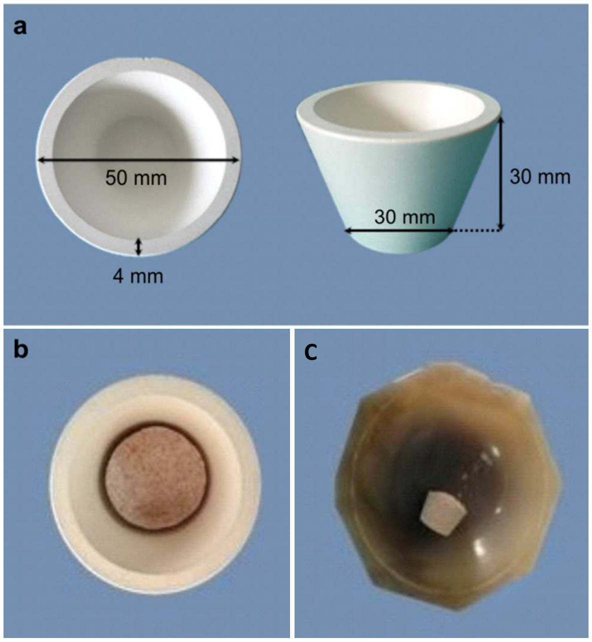

Fig. 1 a. Custom-made BN crucible showing the dimensions; Effect of the BN crucible after oxidation: b. the powder clearly separating from the BN crucible naturally; c. the powder appearing almost as a whole when added into the agate mortar

After this, the mixture was transferred to the BN crucible and placed in a muffle furnace. Then, it was fired at a low temperature of about 700°C to perform pre-oxidation. To obtain accurate pre-oxidation parameters for the retention of sulfur, an orthogonal experiment $L_9(3^4)$ and a sulfur analyser were employed.

Next, the BN crucible was removed from the muffle furnace and cooled to room temperature. Then, the oxidised powder was transferred to the platinum crucible for fusion.

Subsequently, 6 drops of 30 g/L of NH_4Br were added to the powder. Then, the platinum crucible was placed into an automatic fusion machine. After 10 min, the sulfide sample bead was prepared. The sulfur analyser was employed for the purpose of confirming whether the volatilisation of sulfur occurred during fusion.

Finally, fused glass discs were analysed using the WD-XRF spectrometer. Then, calibration curves were obtained. Figure 2 shows the proposed procedure.

Results and Discussion

Pre-oxidation

Thermal analysis. Thermal analysis provides information about the thermal behaviour of the sulfide sample as well as oxidation so as to select a temperature range suitable for retaining sulfur.

Figure 3a shows the TG-DTA curve of GBW07165; reduced sulfur clearly volatilised at approximately 450 °C (A) with a substantial weight loss; that is, oxidation must occur before 450 °C for the retention of sulfur. As shown in Figure 3b, the endotherm at near 260°C (B) corresponded to the melting point of $LiNO_3$, which is equal to that typically reported,[20] and the decomposition of $LiNO_3$ with a weight loss occurred at approximately 600 °C (C). As shown in Figure 3c–D, when the sulfide sample and auxiliaries were mixed together, an exothermic reaction occurred at approximately 300 °C, implying that oxidation occurs immediately after the melting of $LiNO_3$.[3] This result is in good agreement with the oxidation temperature required with sulfide samples for the retention of sulfur, as shown in Figure 3a-A. From this perspective, it is clear that the experimental combination of the oxidant and flux used in this study can retain the reduced sulfur.[21]

Effect of the BN crucible. As the oxidised powder is transferred from the BN crucible to the platinum crucible for fusion, the powder should be easily and completely separated from the BN crucible. Figure 1b-c shows the effect of the BN crucible after oxidation. The powder clearly separated from the BN crucible naturally after oxidation (Figure 1b), and it appeared almost as a whole when added into the agate mortar (Figure 1c). Therefore, the BN crucible is very convenient for sample preparation. Besides, the BN crucible is a type of a plastic ceramic material. That is, after its use for a long time, it can be immediately recovered as new by sanding.

Sulfur analysis. A sulfide ore has a very complex composition, as well as its oxidation. To quantitatively retain sulfur, three important factors—temperature, time and dilution ratio—were investigated; for this purpose, the sample powders were tested after oxidation using the sulfur analyser. Data analysis in the form of an orthogonal experiment with the Taguchi $L_9(3^4)$ orthogonal array was employed to obtain the optimal oxidation parameters. [22-24] Table 1 shows the experimental conditions and the corresponding results. By the comparison of the mean values at every level, the following optimal parameters were obtained: temperature, 650 °C; time, 30 min and dilution ratio, 1:30. This result is clearer in Figure 4. [25]

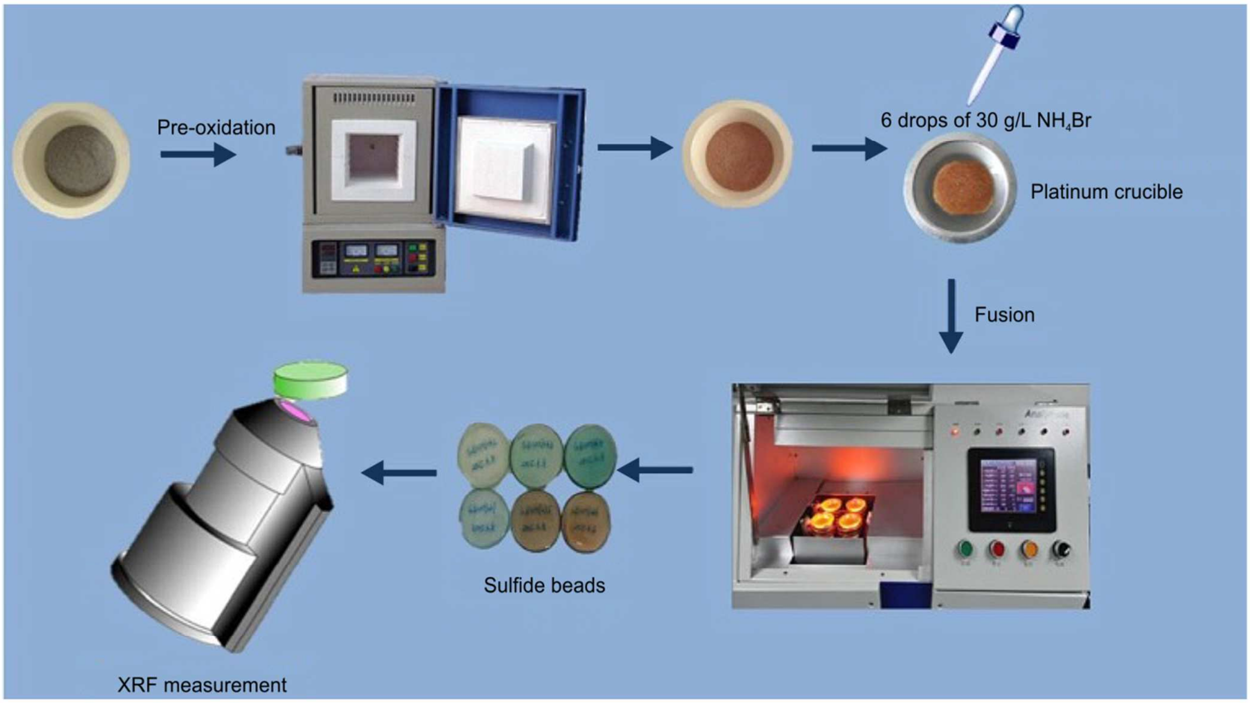

Fig. 2 Pre-oxidation using the BN crucible and XRF measurement

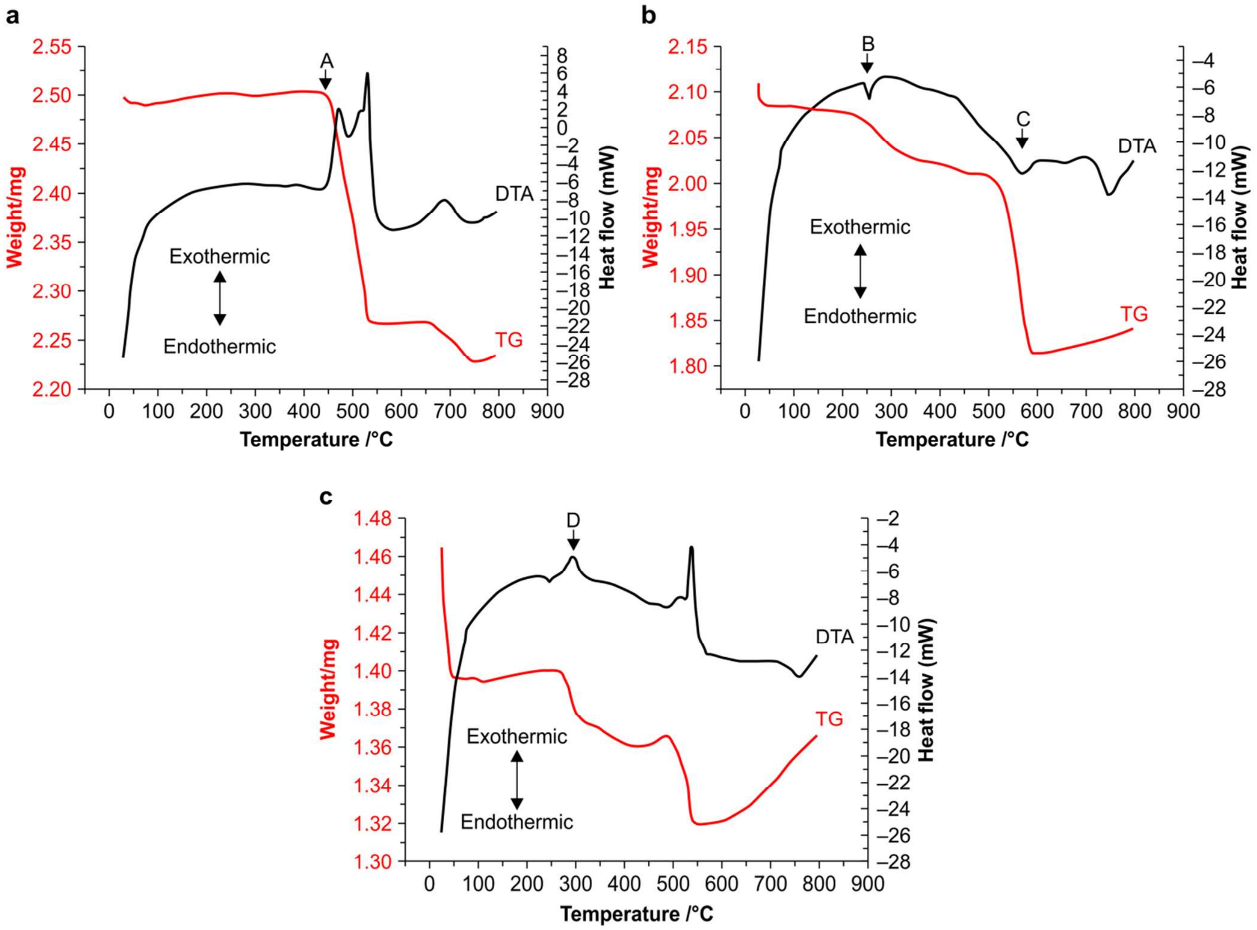

Fig. 3 Differential and gravimetric thermal analysis of a. GBW07165; b. mixture of $LiNO_3$ and $Li_2B_4O_7$; c. mixture of $LiNO_3$, $Li_2B_4O_7$ and GBW07165

For verifying the results and obtaining the final sulfur-retained ratio at the optimal conditions, three reference materials—GBW07165, CAN SU-1B and JZN-1—with different sulfur concentrations were analysed under the optimal parameters. As shown in Table 2, throughout pre-oxidation using $LiNO_3$ and $Li_2B_4O_7$ at a weight ratio of 20:80 under the optimal conditions, the reduced sulfur could be quantitatively reserved. [26]

X-ray diffraction. The sulfur analyser already provided quantitative results. In order to get some qualitative results, qualitative analysis method of chemical analysis by X-ray diffraction was employed. To investigate the phase change during pre-oxidation, as well as to validate the optimum sulfur-retained ratio obtained above, the experimental products obtained from the reference material GBW07165 were analysed. Figure 5a shows the XRD pattern of the reference material GBW07165; the sulfide ore mainly consists of four phases: SiO_2, FeS_2, ZnS, and PbS. This result is in agreement with its certified composition. Figures 5b and 5c show the comparison of the phases of the mixed powder before and after oxidation, respectively.[27] The spectral peak of ZnS disappeared after oxidation and was replaced by the spectral peaks of $LiBO_2$ and Li_2SO_4. That is, the reduced sulfur in the sulfide ore was oxidised to its highest oxidation state SO_4^{2-}.

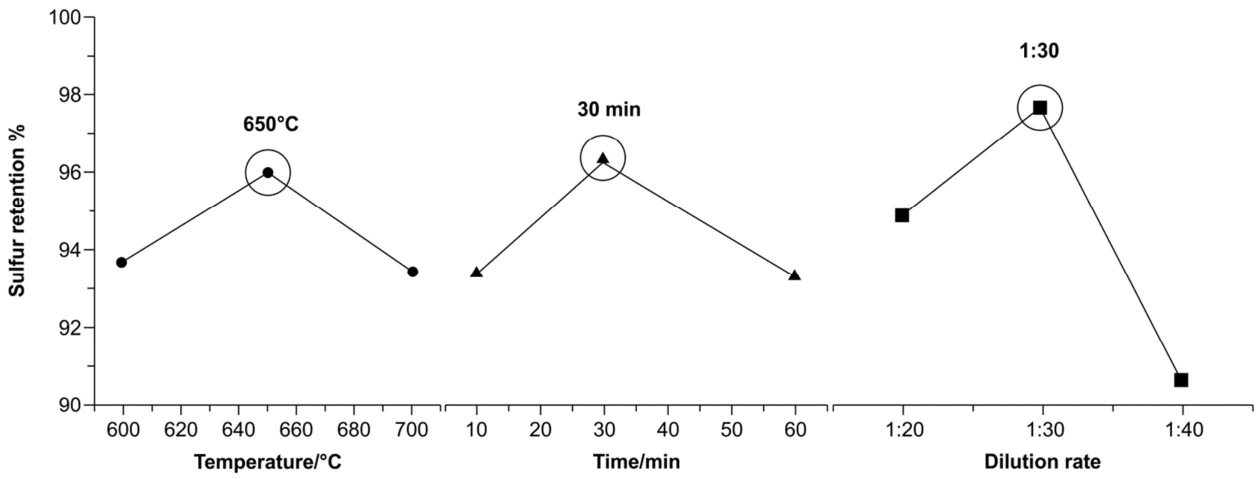

Fig. 4 Effects of temperature, time, and dilution ratio

Table 1 Orthogonal array $L_9(3^4)$ and intuitive analysis table[a]

Experiment	Temperature /℃	Time/min	Dilution ratio	sulfur-retained ratio
1	600	10	1:20	90.18 ± 2.07
2	600	30	1:30	99.88 ± 2.39
3	600	60	1:40	90.83 ± 1.37
4	650	10	1:30	100.27±2.64
5	650	30	1:40	91.11 ± 1.47
6	650	60	1:20	96.48 ± 1.38
7	700	10	1:40	89.89 ± 0.43
8	700	30	1:20	97.73 ± 0.37
9	700	60	1:30	92.60 ± 0.94
mean value 1	93.63 ± 1.94	93.45 ± 1.71	94.80 ± 1.27	
mean value 2	95.95 ± 1.83	96.24 ± 1.41	97.58 ± 1.99	
mean value 3	93.41 ± 0.59	93.30 ± 1.23	90.61 ± 1.09	
range	2.54	2.94	6.97	

[a] n = 3. Uncertainties correspond to one standard deviation.

The appearance of the $LiBO_2$ peak in the XRD spectrum suggests that the addition of the most effective oxidant $LiNO_3$[28] can shift the composition of flux from $Li_2B_4O_7$ to the eutectic point, which is near $LiBO_2$, and then lower the melting point of the flux. Furthermore, this result can be proved by the phase diagram of the Li_2O–B_2O_3 system[29], and $LiNO_3$ and the phase shift contribute to the retention of sulfur. Hence, based on the results above, the proposed pre-oxidation in this study is valid for quantitative retention of sulfur.

Table 2 Sulfur-retained ratio of reference materials using the sulfur analyser[a]

Reference material	Certified value / S % by weight	sulfur-retained ratio /%
GBW07165	29.0 ± 0.4	99.23 ± 2.78
CAN SU-1B	14.14 ± 0.11	100.33 ± 2.34
JZn-1	1.30 ± 0.02	101.38 ± 4.14

[a] n = 3. Uncertainties correspond to one standard deviation.

Fusion

Sulfur analysis. According to literature, several scholars have suggested that sulfur possibly volatilises as Li_2SO_4 during fusion.[2,5] Besides, SO_3 is a mild volatile substance. For eliminating these uncertain factors and understanding the sulfur retention in this step, the sulfur analyser was employed to test the concentration of sulfur in the ground fusion beads. Notably, making a uniform sample bead, which has no cracks and crystallisation, is primary for the analysis work in XRF. In this study, the fusion temperature is 1000 °C, and the time taken to make the beads using the full-automatic bead-making machine is 10 min. Besides, 6 drops of 30 g/L NH_4Br were added on the mixture as releasing agent before fusion. In this study, 13 reference materials were prepared three times using these experimental parameters. The bead-making success rate was close to 95% with no stabilising agent such as SiO_2. Table 3 lists the results obtained from the sulfur retention of reference material GBW07165, CAN SU-1B and JZN-1. The highest uncertainty of JZN-1 is due to its low sulfur concentration after a dilution of approximately 30 times. A good sulfur-retained ratio from fusion implies that sulfur does not volatilise in this fusion method. Thus far, the samples were successfully prepared with no volatilisation of sulfur.

Table 3 Sulfur-retained ratio of reference materials using the sulfur analyser[a]

Reference material	Certified value / S % by weight	Sulfur-retained ratio /%	
		Pre-oxidation	Fusion
GBW07165	29.0 ± 0.4	99.23 ± 2.78	99.56 ± 1.94
CAN SU-1B	14.14 ± 0.11	100.33 ± 2.34	101.3 ± 2.21
JZn-1	1.30 ± 0.02	101.38 ± 4.14	104.86 ± 7.64

[a]n = 3. Uncertainties correspond to one standard deviation.

X-ray diffraction. After fusion, the sample mixture converted into the glass phase, and Figure 5d shows the XRD pattern of the powder from the fusion bead of GBW07165. The spectrum exhibited a big bulge; hence, it is difficult to obtain any information about the phase change such as during oxidation. However, according to the results obtained by Spangenberg[5], the highest temperature at which no loss of either sulfate or sulfur occurred is 1000 °C.

X-ray measurement

Calibration curves were prepared with 10 reference materials listed in Section 2.1.2. The combination of experimental coefficient and theoretical coefficient was employed for fitting the experimental value to each calibration curve and minimising the root-mean-square (RMS) value so as to conform to the following equation:

$$RMS = \sqrt{\frac{\sum(C^{*}-C)^{2}}{n-k}} \qquad (1)$$

Here, C* is the theoretical concentration, C is the calculated concentration, n is the number of included standards and k is the number of coefficients calculated from regression.[30]

Figure 6 shows the calibration curves of SiO_2 and S. By the summary of the analysis results, the limit of detection (LOD) for S was 0.03%, and the limit of quantitation (LOQ) for S was 0.1%. Besides, the relative standard deviation was between 0.1% and 5%. The curves clearly exhibited good correlation, which again verified the sulfur retention result.

The validation standards were then measured using the calibration curve, which were prepared in the BN crucible at a ratio of 20:80 $LiNO_3$ and $Li_2B_4O_7$ for sulfur retention. Table 4 lists the results obtained and their uncertainty.

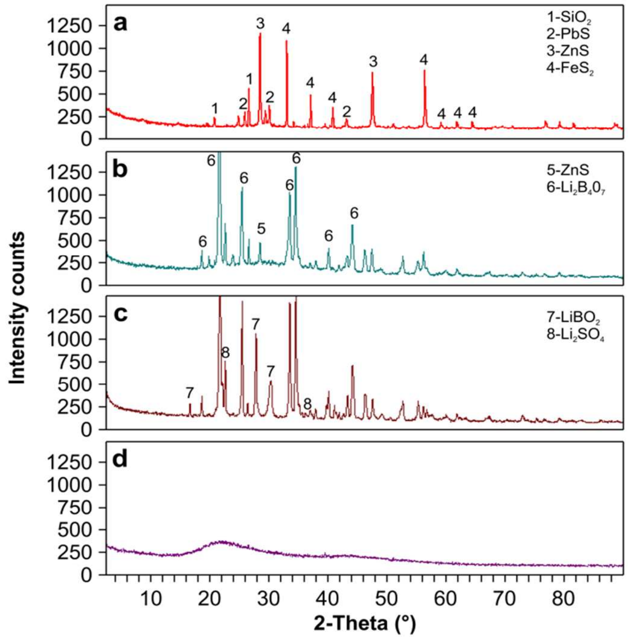

Fig. 5 X-ray diffraction patterns of a. reference material GBW07165; b. mixed powder before oxidation; c. mixed powder after oxidation; d. fused bead of GBW07165

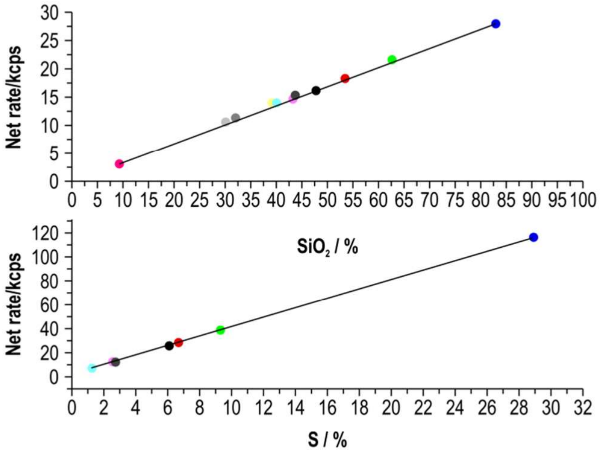

Fig. 6 Calibration curves of SiO_2 and S

Table 4 Analysis of certified reference materials[a]

Constituent	CAN RTS-3A		GBW07163	
	Cert. value/ wt%	Exp. value/ wt%	Cert. value/ wt%	Exp. value/ wt%
SiO_2	39.11 ± 0.43	39.14 ± 0.76	47.90 ± 0.30	47.50 ± 0.70
TiO_2	0.59 ± 0.045	0.59 ± 0.05	/	0.62 ± 0.06
Al_2O_3	9.67 ± 0.13	9.69 ± 0.32	11.2 ± 0.30	10.9 ± 0.33
TFe_2O_3	29.29 ± 0.39	29.35 ± 0.73	12.01 ± 0.43	11.83 ± 0.54
MnO	0.21 ± 0.006	0.21 ± 0.03	0.49 ± 0.05	0.48 ± 0.04
MgO	4.12 ± 0.05	4.26 ± 0.53	1.39 ± 0.07	1.39 ± 0.19
CaO	2.99 ± 0.07	3.00 ± 0.25	4.70 ± 0.20	4.68 ± 0.27
Na_2O	0.92 ± 0.008	0.94 ± 0.17	0.24 ± 0.04	0.23 ± 0.05
K_2O	0.55 ± 0.016	0.56 ± 0.11	3.10 ± 0.30	3.04 ± 0.25
S	9.59 ± 0.12	9.34 ± 0.54	6.74 ± 0.11	6.78 ± 0.40
Cu	0.24 ± 0.003	0.22 ± 0.04	1.05 ± 0.03	1.08 ± 0.06
Pb	***0.02 + 0.0007***	***<LOD***	2.17 ± 0.07	2.15 ± 0.11
Zn	0.29 ± 0.005	0.28 ± 0.10	4.26 ± 0.15	4.33 ± 0.21

[a]n = 3. Uncertainties approximate 95% confidence limits.[31-33]

The experimental results obtained from the validation standard measured by WD-XRF were in good agreement with the certified values, showing that the method proposed in this study exhibits good accuracy and precision. After validation, the elemental composition of the sulfur compounds was determined by WD-XRF using the method proposed in this study and other recognised methods, such as ICP-OES, AAS and gravimetry. The detailed information of the recognised comparison methods that corresponding to every analysis elements was listed in the bottom of table 5.[34-38] According to the results listed in Table 5, our method exhibited good consistency with other techniques. As a result, the content of 13 elements in the sulfide ore was successfully determined simultaneously by the proposed method.

Table 5 Determination of chemical composition of sulfur compounds by WD-XRF and other methods [a]

Constituent	L082-3		S12-5	
	This paper/wt%	Other methods/wt%	This paper/wt%	Other methods/wt%
SiO_2	41.5 ± 0.76	41.21 ± 0.39^1	45.21 ±0.79	45.11 ± 0.26
TiO_2	0.6 ± 0.05	0.58 ± 0.03^2	0.17 ±0.03	0.19 ± 0.02
Al_2O_3	11.42 ±0.34	11.16 ± 0.26^2	5.75 ± 0.25	6.07 ± 0.21
TFe_2O_3	10.99 ±0.53	11.21 ± 0.32^2	16.20 ±0.57	16.43 ± 0.23
MnO	0.31 ± 0.03	0.30 ± 0.002^2	0.13 ± 0.02	0.13 ± 0.004
MgO	3.71 ± 0.47	3.73 ± 0.14^2	0.6 ± 0.10	0.61 ± 0.014
CaO	11.4 ± 0.48	10.95 ± 0.36^2	3.8 ± 0.25	3.71 ± 0.09
Na_2O	1.41 ± 0.26	1.39 ± 0.06^2	0.18 ± 0.04	0.17 ± 0.02
K_2O	1.51 ± 0.15	1.50 ± 0.08^2	1.84 ± 0.16	1.74 ± 0.07
S	4.2 ± 0.28	4.13 ± 0.13^3	14.40 ±0.81	14.56 ± 0.17
Cu	0.54 ± 0.05	0.51 ± 0.04^4	0.11 ± 0.04	0.10 ± 0.02
Pb	1.12 ±0.08	1.10 ± 0.06^4	2.12 ± 0.11	2.17 ± 0.07
Zn	2.18 ± 0.13	2.16 ± 0.05^4	7.04 ± 0.31	6.99 ± 0.12

[a]n = 3. Uncertainties approximate 95% confidence limits.

1: Combination with gravimetry and AAS; alkali fusion with Na_2CO_3/H_3BO_3[34-35]

2: ICP-AES; acid digestion with $HF/HNO_3/HClO_4$[36]

3: Combustion and infrared absorption spectrometry[37]

4: AAS; acid digestion with $HF/HNO_3/HClO_4$[38]

Conclusions

The following conclusions were drawn in this study:

1. A significant number of methods were proposed for the protection of the platinum crucible from contamination when dealing with sulfide samples by the fusion method by WD-XRF. However, the use of the BN crucible for sample preparation in this field has been proposed for the first time. When using the BN crucible during oxidation, the contact of reduced sulfur with the platinum crucible is completely cut off. Besides, the oxidised powder is easily separated from the BN crucible with no adhesion, and it can be restored to new immediately by sanding it.
2. By the use of the sulfur analyser and the Taguchi orthogonal experiment $L_9(3^4)$, the optical oxidation and fusion parameters for quantitative sulfur retention—650 °C, 30 min, 1:30 and 1000 °C—are obtained. The results of sulfur concentration obtained from the sulfur analyser give evidence for quantitative sulfur retention and fill the gaps in this data. The combination of oxidant $LiNO_3$ and flux $Li_2B_4O_7$ at a mass ratio of 20:80 is demonstrated again to be the most suitable flux mixture for sulfur retention. Of course, this combination can also successfully form homogeneous beads. After pre-oxidation, the reduced sulfur is oxidised to Li_2SO_4 according to the XRD result. As long as the fusion temperature is less than 1000 °C, which may be the decomposition temperature of Li_2SO_4, sulfur does not volatilise.
3. The developed methodology based on the fusion technique by WD-XRF using the BN crucible for pre-oxidation can be successfully applied for the analysis of the major elements in sulfide ores as the quantitative analysis of the sulfur concentration is difficult owing to the volatilisation of sulfur and contamination of the platinum crucible. The relative standard deviation lies between 0.1% and 5%, which are equal to the degree of accuracy obtained from rock analysis. Moreover, 13 major elements present in sulfide ores were simultaneously and rapidly measured with precision and safety.

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Notes and references

1 J. Chen and H. P. Li, *Acta Mieralogica Sinica*, 2013, **33**, 351.
2 J. W. Baker, *Advances in X-Ray Analysis,* 1982*,* **25***,* 91.

3 K. Norrish and G. M. Thompson, *X-Ray Spectrometry,* 1990, **19**, 67.

4 J. Gyves and G. H. Li, *Geophysical & Geochemical Exploration Abroad*, 1990, **5**, 58.

5 J. Spangenberg, L. Fontbote and E. Pernicka, *X-Ray Spectrometry,* 1994, **23**, 83.

6 L. G. Sear, *X-Ray Spectrometry,* 1997, **26**, 105.

7 Y. Zhao, *Metallurgical Analysis,* 2001, **21**, 67.

8 L. P. Hao and Z. R. Wang, *Ordnance Material Science and Engineering,* 2002, **25**, 58.

9 M. Norman, P. Robinson and D. Clark, *The Canadian Mineralogist*, 2003, **41**, 293.

10 M. Q. Tang, X. R. Li and M. G. Luo, *Metallurgical Analysis*, 2012, **32**, 55.

11 X. L. Xiao, *Chinese Journal of Inorganic Analytical Chemistry,* 2013, **3**, 41.

12 L. H. Shi and C. S. Yuan, *Jiangxi Building Materials*, 2013, **3**, 251.

13 M. F. Gazulla, M. P. Gomez and M. Orduna, *X-Ray Spectrometry,* 2009*,* **38***,* 3.

14 J. B. Liu and Q. Bo, *Analytical Letters,* 2010, **43**, 836.

15 Q. Tian, W. X. Zhang and J. N. Song, *Rock and Mineral Analysis,* 2012, **31**, 463.

16 M. X. Ling, Y. Liu and H. Zhang, *Analytical Letters*, 2014, **47**, 1598.

17 L. Y. Zhu, Y. S. Liu and Z. C. Hu, *Geostandards and Geoanalytical Research,* 2012, **37**, 207.

18 J. Ahmad, H. Maekawa and H. Takamura, *Journal of Alloy and Compounds,* 2012, **540**, 222.

19 S. Akatsuki, R. Yamanouchi and Y. Nakamoto, *Bunseki Kagaku,* 2008, **57**, 666.

20 G. Q. Liu, L. X. Ma and J. Liu, Chemical property data handbook: inorganic volume, Chemical Industry Press, 2002,352.

21 N. Dannenbauer, P. Constantinidis and I. Fischer, *Zeitschrift fur Anorganische und Allgemeine Chemie* 2015, **641**, 362.

22 B. Adenso-Díaz and M. Laguna, *Operations Research*, 2006, **54**, 99.

23 J. Y. Zhang, H. W. Zhu and Y. Li, *Journal of China University of Petroleum,* 2009, **33**, 105.

24 M. Dargahi, H. Kazemian and M. Soltanieh, *Powder Technology,* 2012, **217**, 223.

25 M. Abud-Archila, D. G. Va´zquez-Mandujano and M. A. Ruiz-Cabrera, *Journal of Food Engineering,* 2008, **84**, 413.

26 R. Sitko, P. Janik and B. Zawisza, *Analytical Chemistry*, 2015, **87**, 3535.

27 X. H. Su, S. Q. Li and J. G. Li, *Journal of the American Ceramic Society,* 2010, **93**, 1904.

28 J. Eastell and J. P. Willis, *X-Ray Spectrometry,* 1990, **19**, 3.

29 M. Loubser, Chemical and physical aspects of Lithium borate fusion, Pretoria: University of Pretoria, 2009.

30 The SuperQ 4.0O Software' help documents.

31 J. R. Sieber, L. L. Yu and A. F. Marlow, *X-Ray Spectrom*, 2005; **34**: 153.

32 A. Ji, S. J. Zhuo, X-ray fluorescence spectrum analysis, Beijing: Science press, 2003, 218.

33 J. R. Sieber, *Advances in X-ray Analysis*, 2002, **45**, 493.

34 S. Terashima, *Bulletin of the Geological Survey of Japan,* 1979, **30**, 37.

35 S. Terashima, T. Yamashige and A. Ando, *Bulletin of the Geological Survey of Japan,* 1984, **35**, 171.

36 S. Terashima, K. Sato and M. Taniguchi, *Geostandards Newsletter,* 2003, **27**, 259.

37 S. Terashima, *Geostandards Newsletter,* 1988, **12**, 249.

38 S. Terashima and A. Ando, *Geostandards Newsletter,* 1987, **11**, 75.