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ORIGINAL RESEARCH ARTICLE

Optimizing X-ray fluorescence spectrometry using fusion sample preparation to quantify ten major and minor elements in manganese ores

Jing-zhi Ma

Central South Institute of Metallurgical Geology, Yichang 443003, Hubei, China; cugedu@163.com

ABSTRACT

A rapid and straightforward method has been devised for direct analysis of SiO_2, Al_2O_3, Fe, MgO, CaO, K_2O, Mn, TiO_2, P, and Zn in manganese ore samples using an X-ray fluorescence spectrometer (XRF). The method employs a glass fusion technique with a flux composed of $Li_2B_4O_7$, $LiBO_2$, and LiF (in a mass ratio of 45:10:5), NH_4NO_3 as an oxidizing agent, and LiBr as a stripping agent. The method's experimental parameters were fine-tuned, and its performance metrics were assessed. The proposed method was used to analyze the certified reference materials GBW07261 to GBW07266, yielding relative standard deviations (RSD, $n = 12$) below 2%. Accuracy was verified using synthetic samples, and the obtained results were in line with the certified values.

Keywords: fusion sample preparation; XRF; manganese ores; condition optimization

Manganese ore is an important industrial raw material for smelting manganese and steel. The content of its elements directly affects the quality of steel products. Usually, Mn is detected. Fe, P, S, SiO_2, etc.[1,2]. Conventional analysis methods mainly include gravimetric method. Volumetric method. Colorimetry, etc.[3–5]. These analytical methods have high accuracy and good reproducibility, but the sample processing is very cumbersome, and the analysis results are easily affected by human factors and reagent quality[6].

As a mature analytical technique, X-ray fluorescence spectrometry (XRF) is widely used in metallurgy. Cement. In petrochemical and semiconductor industries, the determination accuracy of primary and secondary components is comparable to that of chemical analysis methods[7–11]. In this paper, 1:20 flux is used to dilute and melt the samples, which further eliminates the influence of uneven particle size and composition of the samples, greatly reduces the enhanced absorption effect of the matrix and the interference of coexisting elements, and widens the analysis range, which is suitable for the conventional component analysis of manganese ore raw materials.

1. Test part

1.1. Instrument conditions and reagents

XRF-1800 (Shimadzu, Japan): 4.0 kW end window rhodium target X-ray tube, maximum working voltage 60 kV, maximum working current 140 mA, 75 μm beryllium window; vacuum light path, scanning

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angle 7°~148°, positioning reproducibility 0.0001°.

Analymate-V4D high frequency induction melting prototype (Beijing Jingyuan Century Technology Co., Ltd.); platinum crucible (95%Pt + 5%Au); analytical balance (sensing weight 0.1 mg).

$Li_2B_4O_7$-$LiBO_2$-LiF (mass ratio 45:10:5) premium pure mixed flux (Beijing Jingyuan Century Technology Co., Ltd.), NH_4NO_3 solid, LiBr (0.5 g/mL).

GBW07261~GBW07266 (Research Institute of Central South Geological Exploration Bureau, Ministry of metallurgy); GBW07401 (Geophysical and Geochemical Exploration Institute of the Ministry of Geology and mineral resources); H27~H29 (standard sample of manganese ore in Metallurgical Geology).

1.2. Preparation of fusible sheet

Weigh (6.0000 ± 0.0004) g of mixed flux successively after burning at 700 ℃ for 2 h. (0.3000±0.0001) g of manganese ore standard sample baked at 105 ℃ for 2 h and (0.3000 ± 0.0100) g of ammonium nitrate are placed in a 30 mLporcelain crucible, stirred evenly, transferred to a platinum crucible, added 0.5 mLof 0.5 g/mL libr solution, and put the crucible into the melting sample with crucible pliers for melting and sample preparation. Melting sample preparation procedure: preheat at 650 ℃ for 120 s, and then heat up to 950 ℃ for 240 s. The first two stages are mainly to remove C, S, and protect the crucible, finally the temperature is raised to 1050 ℃ to melt for 180 s, cooled, and demoulded.

1.3. Preparation of standard series

The national first-class reference materials GBW07261~GBW07266 of manganese ore are selected to establish the standard calibration curve. In order to improve the representativeness of matrix composition and expand the content range and distribution of some elements, several are selected in matrix composition. The standard samples with characteristics in the content of elements to be measured and some of the above standard samples are mixed with each other in different proportions. After full mixing, several new standard samples are prepared. Each standard sample has a certain representativeness, and forms a set of standard series with a certain gradient and sufficient content range. The content range of calibration curve is listed in **Table 1**.

Table 1. Concentration range of components in calibration samples.

Component	Content range ω/%	Component	Content range ω/%
SiO_2	10.46~42.42	CaO	0.05~19.78
TiO_2	0.063~0.618	MgO	0.10~3.82
Al_2O_3	1.68~11.36	K_2O	0.45~1.80
Fe	1.22~20.99	P	0.04~0.27
Mn	15.74~45.39	Zn	0.018~0.066

1.4. Testing

According to the content of each element in the standard curve, select the highest and lowest two glass samples for condition test, and select the best voltage. Current, test angle and other conditions, and the detection conditions of each element are listed in **Table 2**.

Table 2. Optimal measuring conditions of each element.

Element	Analytical line	Analytical crystal	Collimator	Detector	Voltage/ kv	Electric current /ma	Test angle and time		Background angle and time		Pulse height distribution	
							2θ (°)	t/s	2θ (°)	t/s	LL	HL
Si	Ka	PET	Std	FPC	40	70	108.94	25	111.000	10	20	80
Ti	Ka	Lif	Std	SC	40	70	86.18	30	87.70	10	20	80
Al	Ka	PET	Std	FPC	40	70	144.68	25	147.50	10	20	80
Fe	Ka	Lif	Res	SC	40	70	57.53	25	58.90	10	20	80
Mn	Ka	Lif	Std	SC	40	70	63.00	25	63.70	10	20	80
Mg	Ka	TAP	Sen	FPC	40	70	45.14	25	47.17	10	20	80
Ca	Ka	Lif	Res	FPC	40	70	113.09	25	114.80	10	20	80
K	Ka	Lif	Std	FPC	40	70	136.69	30	139.00	10	20	80
P	Ka	Ge	Std	FPC	40	70	140.94	30	143.00	10	20	80
Zn	Ka	Lif	Std	SC	40	70	41.80	30	42.40	10	20	80

2. Results and discussion

2.1. Optimization of sample preparation factors

2.1.1. Selection of sample preparation method

The commonly used sample preparation methods for XRF analysis of powder samples are tablet pressing method and melting tablet method. The tablet pressing method is simple to operate. Economic, but due to the complex standard samples of this system, there is a serious mineral effect, which leads to a large deviation in the analysis results[12]. Compared with the tablet pressing method, the melting method is more complex in operation, but in the process of melting, it can eliminate the mineral effect and particle size effect. At the same time, through the dilution of flux, the matrix effect is reduced, so that the analysis results with good precision and accuracy can be obtained[12]. Therefore, this paper uses the melting sheet method to determine 10 kinds of main components in manganese ore samples. Secondary element.

2.1.2. Selection of flux type

According to the principle of acid-base reaction, acid-base mixed flux should be used for melting and sample preparation. At the same time, the fused glass sheet should have a certain mechanical strength as far as possible. Stable and not easy to absorb moisture. This paper adopts the mixed reagent of $Li_2B_4O_7$, $LiBO_2$ and LiF is used as the flux, in which the addition of LiF enhances the melting fluidity[13], so that the prepared sample is more uniform, and at the same time, the bubbles are basically exhausted in the melting stage through mechanical rotation.

2.1.3. Selection of flux dilution ratio

The ratio of sample and flux directly affects the molding of sample and the fluorescence intensity of elements. $Li_2B_4O_7$-$LiBO_2$-LiF mixed flux is used respectively, and the mass ratio of flux to sample is 10:1, 15:1, 20:1, 25:1. The same sample was prepared at 30:1, and XRF was measured at the same time. The test results show that when the dilution ratio is less than 15, the fluidity is poor, there are more bubbles, and the damage to the crucible is greater; when the dilution ratio is greater than 20, the glass sheet is easy to leave the crucible, and with the increase of dilution ratio, the fluorescence signal intensity of elements gradually decreases, especially for the determination of light elements. GBW07265 sample is selected for analysis in the test, and **Figure 1** shows Si, Fe, Mn. The relationship between the signal intensity of Ca and the dilution ratio. Through comparison, it is found that when the dilution ratio is 20:1, relatively stable results with certain signal strength can be obtained. Therefore, the flux dilution ratio of 20:1 is adopted in this paper.

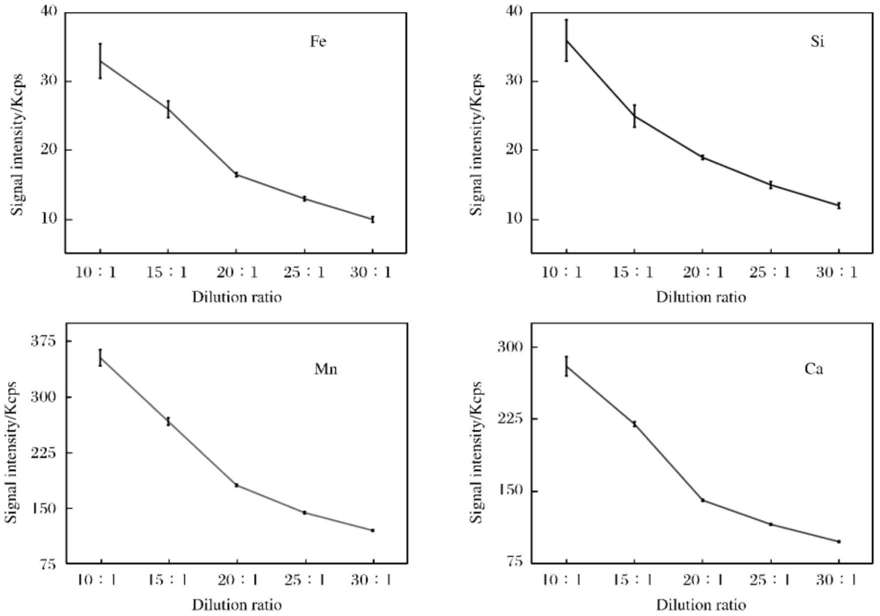

Figure 1. Effect of dilution ratio on signal intensity (*n* = 3).

2.1.4. Selection and dosage of release agent

Commonly used release agents are LiBr, NH4I, KBr and NaI, etc. We do not consider KBr and NaI when determining K and Na, and element I interferes with the primary line of Ti[12], so this paper uses LiBr as the release agent.

Most mold release agents can volatilize in different melting times, but there will still be residues. Therefore, the amount of mold release agent added should not only ensure good fluidity and mold release during the melting process, but also add as little release agent as possible. agent. In the test, 0.1, 0.3, 0.5, 0.7, 0.9 mL of LiBr release agent (0.5 g/mL) were added to the GBW07263 for multiple melting measurements. **Figure 2** shows that the signal intensity of Si, Fe, Mn, and Ca varies with release. Changes in the dosage of the agent. In order to obtain better stability results, 0.5 mL of 0.5 g/mL LiBr was finally selected as the dosage of the release agent.

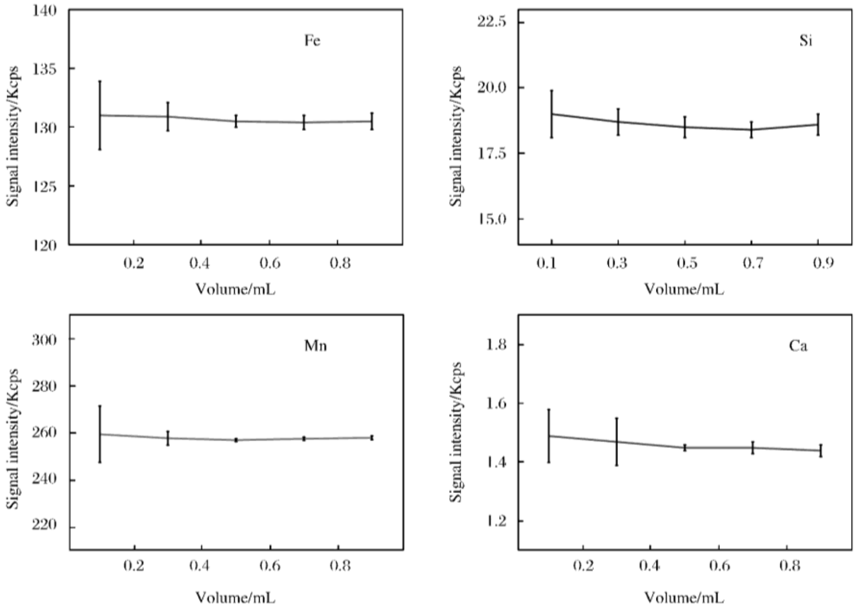

Figure 2. Effect of quantity of mold release agent on signal intensity (*n* = 3).

2.1.5. Selection of melting temperature

At 950 for the same sample. 1000 melt at 1050 and 1100 ℃. It is found that when the melting temperature is lower than 1000 ℃, the molten sample is not uniform enough, and the fluidity of molten liquid is poor in the melting process; the samples prepared at 1050 and 1100 ℃ are smooth, and the molten sheet is not easy to crack. Considering the influence of high temperature on the crucible, 1050 ℃ is selected as the melting temperature in this test.

2.2. Detection limit of the method

The detection limit LLD (instrument detection limit) of each analytical component is calculated according to Equation (1), and the calculation results are listed in **Table 3**.

$$\mathrm{LLD} = \frac{3}{m}\sqrt{\frac{I_\mathrm{b}}{T_\mathrm{b}}} \tag{1}$$

where, m: measurement sensitivity (slope of standard curve); I_b: fluorescence intensity of background; T_b: measurement time of background.

Table 3. Detection limits and quantification limits of components/(μg/g).

Component	**LLD**		**Component**	**LLD**	
	Instrument detection limit	**Method detection limit**		**Instrument detection limit**	**Method detection limit**
SiO_2	45.4	232.7	CaO	51.8	145.2
TiO_2	19.6	45.2	MgO	44.3	92.6
Al_2O_3	18.6	59.8	K_2O	19.5	102.5
Fe	146.5	718.2	P	13.4	21.5
Mn	187.2	835.8	Zn	9.5	19.7

The detection limit of the method is related to the matrix content in the sample. Different samples will have different background intensity due to different component content, so the detection limit is also different. In this paper, the same manganese ore sample is used for melting tablets, and the standard deviation of each component is calculated for 12 consecutive times. The detection limit of this method is 3 times of the standard deviation. The results are listed in **Table 3**.

2.3. Matrix effect and spectral line overlap correction

The enhanced absorption effect of the matrix can be reduced to a certain extent by diluting the molten sample with a large proportion of flux. However, due to the large difference in the content of primary and secondary components in the sample and the wide range, the enhanced absorption effect between some elements is difficult to eliminate, so matrix correction must be carried out. In this test, the matrix correction formula provided by the instrument is used to calculate the corresponding absorption enhancement coefficient and spectral line overlap coefficient. The calculation formula is as follows Equation (2):

$$Wi = (a \times I^2 + b \times I + c) \times (1 + \sum dj \times Wj) - \sum Lj \times Wj, (j \neq i) \tag{2}$$

where: *Wj*: quantitative results of matrix elements; *dj*: absorption influence coefficient; *Lj*: overlapping influence coefficient; *Wi*: quantitative results of corrected elements; *I*: *X*-ray intensity of the corrected element; *a*, *b*, *c*: standard curve constant.

2.4. Precision analysis

According to the sample control method in 1.2, prepare 12 samples of manganese ore standard samples gbw$_0$7263 and gbw$_0$7265 repeatedly, and analyze them according to the measurement conditions in **Table 2**. The statistical results are listed in **Table 4**.

Table 4. Precision test (*n* = 12)/%.

Standard sample	Component	Determine the average value	Standard reference value	SD	RSD
GBW07263	SiO_2	14.51	14.50	0.081	0.56
	TiO_2	0.42	0.43	0.0073	1.69
	AI_2O_3	8.54	8.55	0.050	0.58
	Fe	11.26	11.24	0.036	0.32
	Mn	32.57	32.54	0.094	0.29
	MgO	0.11	0.11	0.0012	1.12
	CaO	0.08	0.08	0.0012	1.53
	K_2O	0.92	0.93	0.0030	0.32
	P	0.20	0.21	0.0042	1.98
	Zn	0.063	0.064	0.0010	1.55
GBW07265	SiO_2	14.18	14.07	0.10	0.73
	TiO_2	0.10	0.10	0.0017	1.72
	AI_2O_3	1.67	1.68	0.010	0.62
	Fe	1.39	1.40	0.017	1.21
	Mn	22.48	22.54	0.099	0.44
	MgO	3.49	3.50	0.030	0.86
	CaO	14.72	14.73	0.14	0.95
	K_2O	0.46	0.46	0.0025	0.55
	P	0.04	0.04	0.0007	1.87
	Zn	0.017	0.018	0.0003	1.69

2.5. Accuracy analysis

In order to verify the accuracy and practicability of this method, manganese ore standard sample gbw$_0$7263 was tested. GBW$_0$7264. Gbw$_0$7265 and mixed standard samples were tested, and the analysis results are listed in **Table 5**. It can be seen from **Table 5** that the test conditions selected in this paper are used for melting sample preparation, and the samples obtained are analyzed by X-ray fluorescence spectrometer. The results are in good agreement with the standard values, indicating that the test results of this method are accurate and reliable.

Table 5. Accuracy test (*n* = 3).

Element	Sample	SiO_2	TiO_2	Al_2O_3	Fe	Mn	Mgo	CaO	K_2O	P	Zn
GBW07263	Standard reference value	14.50	0.43	8.55	11.24	32.54	0.11	0.08	0.93	0.207	0.064
	Measured value	14.55	0.44	8.58	11.27	32.40	0.12	0.08	0.92	0.207	0.060
GBW07264	Standard reference value	10.46	0.54	8.97	20.99	25.00	0.10	0.05	0.72	0.275	0.048
	Measured value	10.55	0.55	8.96	20.97	24.89	0.11	0.05	0.73	0.274	0.050
GBW07265	Standard reference value	14.07	0.10	1.68	1.40	22.54	3.50	14.73	0.46	0.043	0.018

	Measured value	14.14	0.11	1.71	1.43	22.70	3.50	14.76	0.46	0.044	0.019
MX-1	Standard reference value	39.38	0.44	8.19	2.43	22.78	1.23	1.39	1.80	0.065	0.048
	Measured value	39.45	0.42	8.17	2.41	22.79	1.25	1.40	1.81	0.064	0.049
MX-2	Standard reference value	42.42	0.45	8.59	2.94	18.58	1.63	2.66	1.53	0.078	0.049
	Measured value	42.53	0.45	8.62	2.96	18.74	1.66	2.69	1.50	0.079	0.051
MX-3	Standard reference value	38.55	0.62	11.36	7.44	16.36	0.96	0.90	1.76	0.141	0.066
	Measured value	38.39	0.60	11.32	7.49	16.29	0.94	0.88	1.77	0.139	0.069

Remarks: MX-1 (GBW07261:GBW07401 = 1:1); MX-2 (GBW07262:GBW07401 = 1:1); MX-3 (GBW07263:GBW07401 = 1:1).

3. Conclusion

This paper adopts $Li_2 B_4O_7$. A method for the simultaneous determination of 10 major and minor components in manganese ore samples by XRF was established. This method is applicable to a wide range of contents. The accuracy is high, and compared with conventional chemical analysis, the operation is simple and fast. Green and environmental protection, suitable for batch determination of actual samples.

Conflict of interest

The author declares no conflict of interest.

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