XRF1101 - Fusion bead analysis for refractories using application package Refractory series

Introduction

X-ray fluorescence (XRF) analysis is widely used in a number of fields, including quality control and research & development, due to its high degree of accuracy and extremely simple sample preparation. Quantitative analysis with XRF spectrometry requires reference materials in order to generate calibration curves.

The fusion method in X-ray fluorescence (XRF) analysis is an effective sample preparation technique for getting accurate analysis results of powder samples, since the technique eliminates heterogeneity due to grain size and mineralogical differences.
Rigaku provides analysis solution for various refractories by the fusion method.

This application note introduces Application Packages "Refractory" series and demonstrates repeatability of this analysis.

Application Package

Rigaku Application Packages are products which are designed to enable unexperienced users to start up quantitative analysis easily.
The Application Packages "Refractory" series are targeted at XRF analysis of five refractory materials (silica, clay, magnesia, chrome-magnesia and zircon-zirconia) by the fusion method. Table 1 shows the list of the Application Packages "Refractory" series.

Table 1: List of the Application Packages "Refractory" series.

The contents of the package are as follows:

- Calibration standards
    - Series of reference materials
      (powder in a bottle, 10g / material)

- Drift correction samples
    - Two fusion beads

- Installation CD
    - temporary calibration curves (calibration constants)

    - correction coefficients

    - measurement conditions

    - other application setting

- Instruction manual

Users can make fused beads of calibration standards using their own fusion machine, which will be used for analysis samples. Quantitative application, including temporary calibration curves, measurement conditions, correction coefficients, drift correction setting, is installed in the system by running the installation CD.

After running the fused beads of the calibration standards, regression calculation is automatically carried out, where the calibration formulas follow the temporary calibration curves.

The procedure is shown step-by-step in the instruction manual.

Instrument

The Application Packages "Refractory" series are applicable to Rigaku sequential wavelength-dispersive (WD) XRF spectrometer, ZSX Primus IV, ZSX Primus IVi and ZSX Primus III NEXT. In the case of ZSX Primus III NEXT, the optional Ge crystal is required.

Calibration and CRMs

Certified reference materials (CRMs) by The Technical Association of Refractories, Japan are used in the packages. The number of the CRMs included in each package is shown in Table 1.

Table 1: List of the Application Packages "Refractory" series

Material	Reference materials included	Number of CRMs	Analysis components
Clay	JRRM 121 – 135	15	SiO_2 Al_2O_3 Fe_2O_3 TiO_2 MnO CaO MgO Na_2O K_2O P_2O_5 Cr_2O_3 ZrO_2
Silica	JRRM 201 – 210	10	SiO_2 Al_2O_3 Fe_2O_3 TiO_2 MnO CaO MgO Na_2O K_2O
Magnesia	JRRM 401 – 410	10	SiO_2 Al_2O_3 Fe_2O_3 CaO MgO TiO_2 MnO P_2O_5
Chrome-Magnesia	JRRM 501 – 512	12	SiO_2 Al_2O_3 Fe_2O_3 TiO_2 MnO CaO MgO Cr_2O_3 P_2O_5
Zircon-Zirconium	JRRM 601 – 610	10	SiO_2 Al_2O_3 Fe_2O_3 TiO_2 CaO MgO Na_2O K_2O P_2O_5 Cr_2O_3 ZrO_2 HfO_2

Note) "High-alumina" package used to be available. The reference materials of alumina refractory are out of stock.

Calibration was established for each material. The calibration summary is shown in Tables 2 – 6. Theoretical alpha correction is applied if required.

The accuracy of calibration was calculated by the following formula:

$$Accuracy = \sqrt{\frac{\sum_i (C_i - \hat{C}_i)^2}{n-m}}$$

C_i: calculated value of standard sample
$\hat{C}_i$: reference value of standard sample
n : number of standard samples.
m: degree of freedom (linear 2, quad. 3)

Sample preparation

Powder samples, pre-dried at 110°C, were fused at 1100°C-1200°C, where the weight ratio of sample to flux is 1:10, except for Chrome-Magnesia series, where the ratio is 1:20. The sample and flux should be weighed to 0.1 mg exactly.

Lithium tetraborate ($Li_2B_4O_7$) is used as flux.

Repeatability test

A repeatability test, by 10-time consecutive runs, was performed using the ZSX Primus IV with a 4 kW Rh target X-ray tube.

The test results are shown in Tables 2 – 6.

Table 2: Calibration summary and repeatability test results of "Clay" series. (unit: mass%)

Component	Concentration range	Accuracy	Repeatability test results					
			Content	Std. dev.	R.S.D.	Content	Std. dev.	R.S.D.
SiO_2	37.33 − 86.35	0.25	80.47	0.038	0.05%	63.61	0.031	0.05%
Al_2O_3	6.077 − 49.01	0.22	13.79	0.014	0.10%	29.91	0.016	0.05%
Fe_2O_3	0.248 − 4.459	0.019	3.98	0.002	0.05%	1.92	0.002	0.10%
TiO_2	0.056 − 3.362	0.15	0.45	0.003	0.67%	0.68	0.004	0.59%
MnO	0.008 − 0.370	0.003	0.015	0.001	6.7%	0.024	0.0005	2.1%
CaO	0.109 − 2.804	0.055	0.049	0.0006	1.2%	0.146	0.0010	0.68%
MgO	0.084 − 3.107	0.016	0.67	0.006	0.90%	0.98	0.008	0.82%
Na_2O	0.072 − 3.208	0.022	0.30	0.007	2.3%	0.60	0.010	1.7%
K_2O	0.109 − 3.140	0.013	0.15	0.0008	0.53%	1.82	0.002	0.11%
P_2O_5	0.046 − 4.905	0.048	(0.048)	0.0007	1.5%	(0.053)	0.0008	1.5%
Cr_2O_3	0.010 − 1.278	0.0096	(0.018)	0.0009	5.0%	(0.037)	0.0011	3.0%
ZrO_2	0.008 − 1.119	0.015	(0.076)	0.0011	1.4%	(0.076)	0.0014	1.8%

Table 3: Calibration summary and repeatability test results of "Silica" series. (unit: mass%)

Component	Concentration range	Accuracy	Repeatability test results		
			Content	Std. dev.	R.S.D.
SiO_2	84.43 – 97.80	0.292	96.20	0.027	0.03%
Al_2O_3	0.163 – 9.723	0.020	0.77	0.003	0.39%
Fe_2O_3	0.064 – 3.975	0.018	0.53	0.001	0.19%
TiO_2	0.005 – 0.567	0.003	0.190	0.0015	0.79%
MnO	0.001 – 0.147	0.001	0.010	0.0004	4.0%
CaO	0.301 – 4.200	0.010	1.810	0.0025	0.14%
MgO	0.020 – 0.789	0.007	0.050	0.0070	14%
Na_2O	0.021 – 1.015	0.017	0.050	0.0035	7.0%
K_2O	0.006 – 0.948	0.090	0.090	0.0010	1.1%

Table 4: Calibration summary and repeatability test results of "Magnesia" series. (unit: mass%)

Component	Concentration range	Accuracy	Repeatability test results					
			Content	Std. dev.	R.S.D.	Content	Std. dev.	R.S.D.
SiO_2	0.188 – 8.144	0.025	1.55	0.005	0.29%	0.89	0.004	0.44%
Al_2O_3	0.058 – 8.106	0.024	0.97	0.003	0.30%	0.23	0.002	0.91%
Fe_2O_3	0.050 – 5.050	0.015	4.63	0.002	0.04%	0.29	0.001	0.21%
CaO	0.208 – 4.805	0.019	2.28	0.003	0.12%	1.66	0.002	0.09%
MgO	81.24 – 99.08	0.20	90.6	0.06	0.07%	96.7	0.06	0.07%
TiO_2	0.003 – 0.054	0.0035	0.03	0.001	3.3%	0.015	0.0008	5.3%
MnO	0.010 – 0.074	0.0009	0.14	0.0004	0.29%	0.001	0.0003	30%
P_2O_5	0.015 – 0.120	0.0020	(0.014)	0.0003	2.1%	(0.012)	0.0003	2.5%

Table 5: Calibration summary and repeatability test results of "Chrome-Magnesia" series. (unit: mass%)

Component	Concentration range	Accuracy	Repeatability test results					
			Content	Std. dev.	R.S.D.	Content	Std. dev.	R.S.D.
SiO_2	0.928 – 10.57	0.091	2.59	0.005	0.21%	3.01	0.006	0.21%
Al_2O_3	2.926 – 29.26	0.10	14.7	0.02	0.16%	12.3	0.03	0.24%

Fe_2O_3	1.022 – 27.09	0.11	10.3	0.01	0.05%	7.2	0.01	0.07%
TiO_2	0.006 – 1.205	0.0060	0.140	0.0026	1.9%	0.130	0.0026	2.0%
MnO	0.006 – 0.176	0.0024	0.11	0.001	1.0%	0.11	0.001	1.0%
CaO	0.071 – 4.063	0.016	1.17	0.002	0.15%	1.54	0.002	0.12%
MgO	10.57 – 87.72	0.24	53.5	0.07	0.12%	61.8	0.06	0.10%
Cr_2O_3	2.832 – 52.26	0.066	17.2	0.01	0.04%	13.4	0.01	0.04%
P_2O_5	0.004 – 0.036	0.0029	(0.01)	0.001	6.0%	(0.02)	0.001	6.0%

Table 6: Calibration summary and repeatability test results of "Zircon-Zirconia" series. (unit: mass%)

Component	Concentration range	Accuracy	Repeatability test results					
			Content	Std. dev.	R.S.D.	Content	Std. dev.	R.S.D.
SiO_2	0.263 – 45.70	0.13	0.2	0.002	1.0%	32.7	0.02	0.06%
Al_2O_3	0.078 – 6.933	0.030	0.08	0.02	2.0%	0.33	0.002	0.61%
Fe_2O_3	0.092 – 2.861	0.0044	0.064	0.0008	1.3%	0.060	0.0007	1.2%
TiO_2	0.099 – 0.934	0.021	0.20	0.004	1.8%	0.25	0.004	1.6%
CaO	0.021 – 5.586	0.025	1.50	0.002	0.13%	0.04	0.001	1.8%
MgO	0.017 – 5.304	0.037	3.42	0.010	0.29%	0.05	0.005	10%
Na_2O	0.004 – 2.034	0.024	(0.08)	0.0035	4.4%	0.02	0.003	15%
K_2O	0.002 – 1.942	0.0024	(0.004)	0.0005	13%	0.03	0.001	2.0%
P_2O_5	0.007 – 1.997	0.086	(0.017)	0.0009	5.3%	0.12	0.003	2.1%
Cr_2O_3	0.003 – 3.069	0.0062	(0.016)	0.0010	6.3%	(0.011)	0.0011	10%
ZrO_2	48.74 – 92.08	0.28	92.7	0.05	0.05%	66.2	0.03	0.05%
HfO_2	0.987 – 1.592	0.0091	1.63	0.007	0.43%	1.30	0.006	0.46%

Conclusion

Application Package "Refractory" series, provided by Rigaku, enable users to easily start up fusion bead analysis of refractory materials and to obtain reliable analysis results without high expertise to calibration XRF spectrometers. Since the packages include powder of CRMs, fusion beads of the calibration standards can be made applying exactly the same sample preparation as used for analysis samples.

Related products

ZSX Primus III NEXT

Affordable, high-end, tube-above Industrial WDXRF for the analysis of solid samples

ZSX Primus IV

High power, tube above, sequential WDXRF spectrometer with new ZSX Guidance expert system software

ZSX Primus IVi

High-power, tube-below, sequential WDXRF spectrometer with new ZSX Guidance expert system software