Application Note WDXRF1058

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XRF1058 - Quantitative analysis of dolomite and limestone by pressed powder method with Supermini200

Introduction

Both dolomite and limestone are important mineral resources used in various industries such as cement, electronics, iron manufacturing, glass, paper and pulp, agriculture. Each industry has particular interests in contents and components. For example in the cement industry, dolomite and limestone are sources of Ca. In iron manufacturing, Ca acts as an absorber of impurities like Si, S and P, and Mg protects the furnace walls from corrosive elements like S and P. In the glass industry, low content of Fe is preferred because Fe can color glass.

X-ray fluorescence (XRF) analysis quickly and easily offers precise elemental analysis results allowing control of the components in the product during the manufacturing process.

This application note demonstrates the excellent performance of Supermini200 for the analysis of dolomite and limestone.

Instrument

The Supermini200 is a benchtop sequential wavelength dispersive XRF (WDXRF) spectrometer designed specifically to deliver excellent performance while eliminating conventional installation requirements such as cooling water, special power supply and large floor space. By selecting the optional sealed proportional counter instead of the gas flow proportional counter, requirement of P10 gas can be eliminated as well, realizing a truly utility free WDXRF instrument. Featuring a unique air-cooled 200W X-ray tube, two detectors, three analyzing crystals with selectable vacuum or helium environment, the Supermini200 can analyze elements from oxygen to uranium.

The Windows®-based software used to operate the Supermini200 shares the same platform running Rigaku's popular high-power WDXRF ZSX family instruments. This means that it has the same advanced algorithms, multiple language support and an intuitive user-friendly interface.

Sample Preparation

The samples were ground in a tungsten carbide container for two minutes. The sample to binder ratio is 4.2 g to 0.42 g. Each ground sample mixed with binder (Chemplex Spectro Blend® No.660) was pelletized using an aluminum ring (inner diameter : 32 mm) under the pressure of 150 kN.

Measurement and calibration

Measurements were performed on the Supermini200 for SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, SO_3, Na_2O, K2O, TiO_2, P_2O_5 and MnO. Measurement conditions are shown in Table 1.

Table 1: Measurement conditions

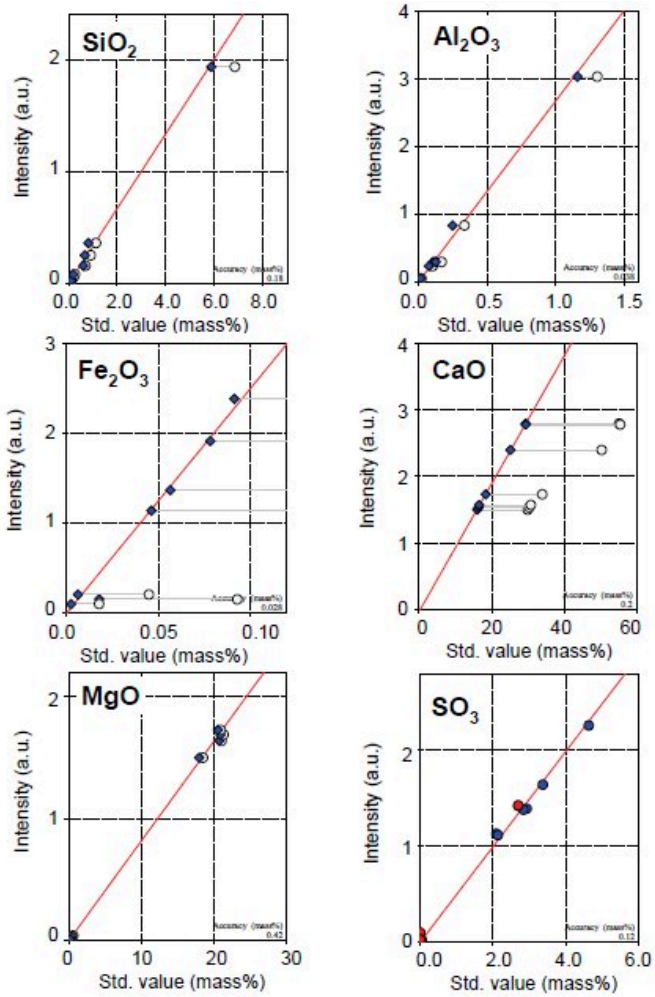
Element	**Si**	**Al**	**Fe**	**Ca**
Line	Kα	Kα	Kα	Kα
kV-mA	50-4.00	50-4.00	50-4.00	50-4.00
Primary Filter	OUT	OUT	OUT	OUT
Slit	Std	Std	Std	Std
Crystal	PET	PET	LiF(200)	PET
Detector	PC	PC	SC	PC
Time Peak (s)	20	20	40	10
BG (s)	10x2	10x2	20	4x2
Element	**Mg**	**S**	**Na**	**K**
Line	Kα	Kα	Kα	Kα
kV-mA	50-4.00	50-4.00	50-4.00	50-4.00
Primary Filter	OUT	OUT	OUT	Al40
Slit	Std	Std	Std	Std
Crystal	RX25	PET	RX25	PET
Detector	PC	PC	PC	PC
Time Peak (s)	40	40	40	40
BG (s)	10x2	20	20x2	20
Element	**Ti**	**P**	**Mn**	
Line	Kα	Kα	Kα	
kV-mA	50-4.00	50-4.00	50-4.00	
Primary Filter	OUT	OUT	OUT	
Slit	Std	Std	Std	
Crystal	LiF(200)	PET	PET	
Detector	SC	PC	PC	

Time Peak (s)	40	40	200
BG (s)	10x2	10x2	100x2

The calibration curves were generated using dolomite and limestone standards shown below:

- National Institute of Standards and Technology (NIST) standards SRM1c and 88b
- Geological Survey of Japan, AIST (GSJ) standards JDo-1 and JLs-1
- Bureau of Analysed Samples Ltd. (BAS) standards BCS-CRM368 and 393.
- European Committee for Iron and Steel Standardization (ECISS) CRM782-1

In order to extend the calibration range, NIST cement standards SRM1881a, 1884a, 1885a, 1886a, 1887a, 1888a and 1889a were added for Na2O and SO3. Ma-trix correction was applied to the components except for SO3 and Na2O. The correction coefficients were calculated theoretically by the fundamental parameter (FP) method. The calibration curves are shown in Figure 1 and the calibration results are listed in Table 2.



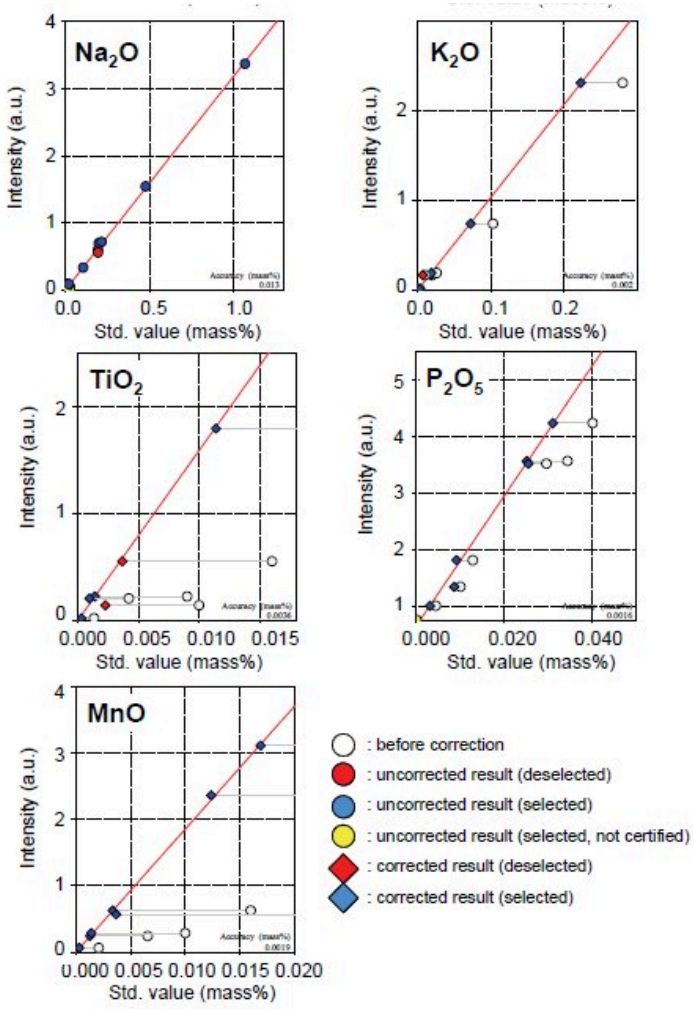


Figure 1: Calibration curves for dolomite and limestone

Table 2: Calibration results (unit : mass%)

Component	Calibration range	Accuracy
SiO_2	0.12 - 6.84	0.18
Al_2O_3	0.0174 - 1.3	0.038
Fe_2O_3	0.0178 - 0.55	0.028
CaO	29.95 - 55.4	0.2
MgO	0.15 - 21.29	0.42
SO_3	0.0397 - 4.622	0.12
Na_2O	0.00194 - 1.068	0.013
K_2O	0.00232 - 0.28	0.002
TiO_2	0.00133 - 0.07	0.0036

P_2O_5	0.0044 - 0.04	0.0016
MnO	0.00209 - 0.081	0.0019

The accuracy of the linear calibration curves are calculated by the following formula:

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

C_i: calculated value of standard sample
$\hat{C}_i$: reference value of standard sample
n : number of standard samples.

Analysis Results

Table 3: Repeatability test results for dolomite (unit : mass%)

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	TiO_2	P_2O_5	MnO
Chemical value	0.266	0.104	0.450	30.34	21.29	0.0397	-	0.0260	0.0042	0.0128	0.081
N=1	0.2725	0.1153	0.4502	29.80	20.91	0.0395	0.034	0.0261	0.0043	0.0131	0.0793
2	0.2677	0.1155	0.4523	29.87	20.95	0.0390	0.048	0.0269	0.0037	0.0132	0.0788
3	0.2679	0.1202	0.4502	29.85	20.96	0.0403	0.046	0.0263	0.0041	0.0151	0.0793
4	0.2711	0.1190	0.4496	29.84	20.89	0.0404	0.036	0.0261	0.0038	0.0142	0.0793
5	0.2709	0.1161	0.4502	29.89	20.97	0.0403	0.033	0.0259	0.0044	0.0138	0.0795
6	0.2714	0.1214	0.4517	29.86	20.86	0.0397	0.047	0.0289	0.0043	0.0144	0.0796
7	0.2664	0.1175	0.4494	29.75	20.91	0.0406	0.043	0.0249	0.0041	0.0137	0.0788
8	0.2691	0.1182	0.4504	29.84	20.93	0.0408	0.034	0.0246	0.0041	0.0141	0.0794
9	0.2688	0.1161	0.4499	29.80	20.89	0.0410	0.048	0.0270	0.0040	0.0147	0.0795
10	0.2699	0.1175	0.4474	29.80	20.97	0.0410	0.039	0.0249	0.0045	0.0147	0.0794
Avg.	0.2696	0.1177	0.4501	29.83	20.92	0.0403	0.041	0.0262	0.0041	0.0141	0.0793
Max.	0.2725	0.1214	0.4523	29.89	20.97	0.0410	0.048	0.0289	0.0045	0.0151	0.0796
Min.	0.2664	0.1153	0.4474	29.75	20.86	0.0390	0.033	0.0246	0.0037	0.0131	0.0788
Range	0.0061	0.0061	0.0049	0.14	0.11	0.0020	0.015	0.0043	0.0008	0.0020	0.0008
Std. dev.	0.0019	0.0020	0.0013	0.04	0.04	0.0007	0.006	0.0013	0.0003	0.0007	0.0003
RSD %	0.71	1.74	0.29	0.14	0.17	1.66	15.15	4.85	6.15	4.66	0.35

Table 4: Repeatability test results for limestone (unit : mass%)

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	TiO_2	P_2O_5	MnO

Chemical value	0.12	0.0207	0.0178	55.09	0.606	0.0307	0.00194	0.00297	0.002	0.0295	0.00209
N=1	0.1222	0.0249	0.0165	54.23	0.51	0.0288	N.D.	0.0034	0.0024	0.0298	0.0025
2	0.1217	0.0238	0.0173	54.18	0.51	0.0300	N.D.	0.0027	0.0024	0.0297	0.0023
3	0.1236	0.0226	0.0174	54.32	0.52	0.0281	N.D.	0.0027	0.0026	0.0313	0.0023
4	0.1219	0.0255	0.0178	54.42	0.52	0.0299	N.D.	0.0034	0.0025	0.0307	0.0028
5	0.1205	0.0240	0.0167	54.28	0.51	0.0289	N.D.	0.0043	0.0026	0.0295	0.0024
6	0.1184	0.0257	0.0167	54.34	0.53	0.0288	N.D.	0.0038	0.0021	0.0288	0.0027
7	0.1218	0.0234	0.0165	54.32	0.51	0.0295	N.D.	0.0026	0.0022	0.0307	0.0026
8	0.1219	0.0242	0.0171	54.33	0.52	0.0290	N.D.	0.0035	0.0024	0.0298	0.0023
9	0.1202	0.0244	0.0164	54.18	0.53	0.0287	N.D.	0.0034	0.0021	0.0317	0.0027
10	0.1193	0.0234	0.0175	54.29	0.52	0.0281	N.D.	0.0031	0.0025	0.0310	0.0025
Avg.	0.1212	0.0242	0.0170	54.29	0.52	0.0290	-	0.0033	0.0024	0.0303	0.0025
Max.	0.1236	0.0257	0.0178	54.42	0.53	0.0300	-	0.0043	0.0026	0.0317	0.0028
Min.	0.1184	0.0226	0.0164	54.18	0.51	0.0281	-	0.0026	0.0021	0.0288	0.0023
Range	0.0052	0.0031	0.0014	0.25	0.02	0.0019	-	0.0017	0.0005	0.0029	0.0006
Std. dev.	0.0016	0.0010	0.0005	0.08	0.01	0.0007	-	0.0005	0.0002	0.0009	0.0002
RSD %	1.28	4.00	2.82	0.14	1.16	2.27	-	15.90	7.71	3.01	8.07

N.D. : Not Detected (below the Lower Limit of Detection, LLD)

Repeatability tests for dolomite and limestone were carried out and the results are shown in Table 3 and 4. The standard deviations for both major and minor components are very small.

Conclusions

The results show that high precision analysis of elements in dolomite and limestone can be performed using the benchtop WDXRF spectrometer Supermini200. The calibration curves obtained using the theoretical alpha corrections show good linearity by pressed powder method for both major and trace components.

Supermini200 is a benchtop spectrometer with a small footprint and is able to be operated with only a wall power outlet. Since Supermini200 is not site-specific, it has the great advantage that it can be installed any-where, and is therefore particularly suited for mining sites or small laboratories.

Related products

Supermini200

Benchtop tube below sequential WDXRF spectrometer anal
yzes O through U in solids, liquids and powders