A NEW R.I. SOURCE EXCITING EDXRF ANALYSER

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Abstract - A source exciting EDXRF Analyser was developed. It has advantage of simple structure, minimal routine maintenance and low cost. The microprocessor controlled multichannel peak-height-analyzer and energy dispersive technique is adopted. Proportional counters are employed as detectors. Elements from Al through U can be analysed with air environment. It has been successfully applied to analysis of cement rawmix, alumina and zinc slag etc..

Key words: X-ray, fluorescence, energy dispersive

INTRODUCTION

R.I. X-ray fluorescence analyzer has advantages of simple structure, minimal routine maintenance and low cost. But it has two problems in technique. One is analysis of light elements, another is analysis of neighbouring elements. Since it came out in 60's, scientists have worked on these problems. Si(Li) detector can be used to resolve the problems. But it must be cooled by liquid nitrogen and it is very expensive. The advantages of R.I. XRF will be lost if Si(Li) detector is employed. Scientists try to analyze multielements including light elements and neighbouring elements with proportional gas counter because of its small size, low cost and non-maintenance. To adopt proportional gas counter as a detector, three problems must be resolved.

1. Fluorescence X-ray of light elements such as Al, Si is strongly absorbed by window of the counter and air between detector and sample. The gas flow counter with window of plastics film couple of μm thick can improve detecting efficiency of light elements such as Al, Si. But a gas supply device is necessary and pressure, flow and temperature of gas must be carefully controlled. Of course, the structure will be complex and difficult to maintenance. It will be very difficult to make it stable and reliable. Also, flow counter has poor resolution (Mnk: 18%). It is difficult to meet the needs of neighbouring elements analysis.

2. Analysis of neighbouring elements and small peak underneath a big peak. Energy of fluorescence X-ray of neighbouring elements is very closed. The resolution of counter is too poor to separate peaks of neighbouring elements. The overlap is very serious. In the other hand, when a very big peak exists in the spectrum, small peaks will be covered, even be 'drowned' although they are not neighbouring elements.

3. Count rate effect. There are two kind of effects. One is the peak shape variation effect. the resolution gets poor. peak gets wide, symmetrization gets poor and background in low energy gets high with count rate increasing. Concentration variation of elements which produces big peak causes serious variation of count rate, further changes peak shape obviously. It causes poor precision and accuracy of small peak. Another is the peak position drift effect. Amplification of the counting gas varies with the count rate and cause peak position drift. It will affect on accuracy. The high count rate is, the more serious the effects are. These two kind of count rate effects brings further complex and difficult of neighbouring elements and small peak. Limiting count rate at a low level can decrease influence of count rate effect (e.g. the analyser made by OUTOKUMPU limiting count rate upto 6000 CPS). But it will increase the measurement time or decrease precision.

STRUCTURE AND PRINCIPLE

Authors developed a new R.I. source exciting EDXRF analyzer adopted R.I. source and close proportional gas counter (Refer to Fig. 1.).

Fig. 1. The picture of the analyzer

Fluorescence X-ray of large range of elements including light elements such as Al, Si, S can be effectively excited and detected. All of three problems mentioned above was resolved. The analyzer has two parts - spectrometer and main computer. The spectrometer consists of double detectors measurement chamber and two-way-puls-processor. Fluorescence X-ray is excited and detected in the chamber. The signal is processed and converted into energy spectrum in the puls processor. The computer display the spectrum, processes it and calculates the concentration with special analytical software then. The analyzer is operated by the keyboard of the computer. Structure and principle of each part as follows.

1. Air environment measurement chamber with double detectors The chamber consists of light element detector, double source weight element detector, sample supporter and safety shell. Both of light element detector and weight element detector has their respective source, counter, preamplifier and high voltage power supply. There are two sample pools on the sample support. They are respectively with their window of counters. After powder sample is pelletized into specimens, put them into two pools to analyze light elements and weight elements simultaneously. Sources irradiate specimens downward to prevent the window of counters from pollution of powder of sample. Fluorescence X-ray of specimens is detected by two counters. Their signals are transferred to the puls processor after preamplified. The chamber also can be inverted to analyze specimen in sample cup. The chamber has three main technical characteristics. 1). In the light element detector, special made thin window, high resolution close proportional gas counter is adopted. Thickness of its Be window is 25 μm and effective diameter is 10-12 mm. It has higher detective efficiency to AlK, SiK. The resolution is 14-16% (MnK). It is good for neighbouring elements analysis. 10-30 mci Fe-55 ring source is used to get higher exciting efficiency to light elements. carefully geometric distribution designing of source, counter and specimen gives maximum detect efficiency to light elements. So that, light elements such as Al, Si, P, S can be effectively analyzed in air environment. Vacuum is not necessary. 2) There are two point sources in the double sources weight element detector. One is a 20-30 mci Pu-238 source and another is a 10-30 mci Am-241 source. They are located at the edge of window of the counter and can be selected by a shutter. Pu-238 is used to analyze K series of middle weight elements and L series of weight elements; Am-241 to K series of weight elements. The counter has 0.2 mm thickness 22-24 mm effective diameter Be window, resolution is 14-16% (MnK). Xe is used as counting gas. this double sources structure not only extends measurement range of weight elements but also simplifies the structure of the analyzer. 3). Low noise electric-charge-sensitive preamplifier is adopt for both detectors. It gives best resolution and decreases the high voltage of counter while noise signal is low enough (less than 0.7 Kev). Best high voltage is 480-520 V for light element detector and 670-720 V for weight element detector.

2. Two-way-puls-processor consists of two-way-amplifier, two-way-ADC, single-chip microcomputer and low voltage power supply. The signals from two detectors are amplified, shaped and filtered by two-way-amplifier. The puls which comes from the two-way-amplifier is analyzed and digitized in the two-way-ADC. The single-chip microcomputer controls ADC and acquires energy spectrum. Acquired spectrum is transferred to main computer by RS-232 serial interface.

The main characteristics of two-way-puls-processor are listed as follows. 1). Two ways work simultaneously. It improves the efficiencies and shortens measurement period. 2). There are 512 channels in each way of the two-way-ADC. It corresponds to the resolution of the counter. It makes the spectrum precise enough while engaged memory is not too large and calculating period is not too long. 3). Single-chip microcomputer and the main computer combines configuration of foreground and background. Foreground single-chip microcomputer acquires the spectrum itself and background main computer processes the spectrum acquired simultaneously.

3. Main computer is IBM PC compatible with coprocessor. The special analytical software is named WL. Due to poor resolution and count rate effect of the counter, distinctive deconvolution technique is used to calculate the intensities of fluorescence X-rays of each element and experiential coefficients method is used to calculate concentration of each element or its oxide in WL software.

Here is the main characteristics of deconvolution technique involved. 1). The overlapped peaks are fitted by non-linear-least-squares fitting with pure element spectra. The background is also subtracted. 2). Peak position orientation technique is adopted to calculate the peak position of each element. The count rate peak position effect, and temperature-dependent and time-dependent peak position drift are corrected based on that. 3). Count rate - peak shape effect caused by big peak in spectrum are corrected automatically.

APPLICATION

Aforementioned analyzer has been applied to industrial analysis of cement, metallurgy, mining and precious metals products in China. Analysis of Portland cement rawmix and alumina is given as examples here.

TABLE 1. Results of Portland cement rawmix analysis

Sample No.	Method	CaO	Fe ₂ O ₃	SiO ₂	Al ₂ O ₃	SO ₃	K ₂ O	TiO ₂
1	Chemical	45.63	1.68	11.81	2.87	0.08	0.33	0.15
	Analyzer	45.70	1.71	11.75	2.76	0.09	0.28	0.14
	Difference	+0.07	+0.03	-0.06	-0.11	-0.01	-0.05	-0.01
2	Chemical	43.85	2.94	13.13	3.16	0.18	0.42	0.17
	Analyzer	43.84	2.92	12.99	3.16	0.18	0.46	0.17
	Difference	-0.01	-0.02	-0.14	0.00	0.00	+0.04	0.00
3	Chemical	43.81	2.34	13.33	3.37	0.12	0.48	0.18
	Analyzer	43.82	2.40	13.49	3.31	0.13	0.46	0.19
	Difference	+0.01	+0.06	+0.16	-0.06	+0.01	-0.02	+0.01
4	Chemical	44.59	3.06	12.11	2.86	0.20	0.40	0.15
	Analyzer	44.50	3.01	11.98	2.92	0.19	0.38	0.16
	Difference	-0.09	-0.05	-0.13	+0.06	-0.01	-0.02	+0.01
5	Chemical	46.27	2.56	10.33	2.44	0.15	0.31	0.13
	Analyzer	46.23	2.65	10.23	2.47	0.17	0.31	0.13
	Difference	-0.04	+0.09	-0.10	+0.03	+0.02	0.00	0.00
6	Chemical	45.40	2.65	11.31	2.65	0.17	0.39	0.14
	Analyzer	45.24	2.71	11.33	2.76	0.17	0.39	0.15
	Difference	-0.16	+0.06	+0.02	+0.11	0.00	0.00	+0.01
Average Difference		0.06	0.05	0.10	0.06	0.01	0.02	0.01

Measurement time was 15 min.

TABLE 2. Results of alumina analysis

Sample No.	Method	Al2O3	SiO2	P2O5	K2O	CaO	TiO2	Fe2O3
1	Chemical	79.15	1.63	0.052	0.060	0.041	1.89	1.34
	Analyzer	78.64	1.44	0.040	0.004	0.041	1.89	1.39
	Difference	+0.51	-0.19	-0.012	-0.056	0.000	0.00	+0.05
2	Chemical	71.25	3.94	0.100	0.440	0.065	1.74	5.42
	Analyzer	71.60	4.08	0.084	0.485	0.061	1.69	5.47
	Difference	+0.35	+0.14	-0.016	+0.045	-0.004	-0.05	+0.05
3	Chemical	67.34	14.16	0.052	1.800	0.065	1.55	0.49
	Analyzer	67.51	14.18	0.061	1.860	0.061	1.69	0.65
	Difference	+0.17	+0.02	+0.009	+0.060	-0.006	+0.14	+0.16
4	Chemical	59.25	20.56	0.027	0.780	0.075	2.19	1.67
	Analyzer	59.37	20.30	0.017	0.870	0.077	2.24	1.63
	Difference	+0.12	-0.26	-0.010	+0.090	+0.002	+0.05	-0.03
5	Chemical	71.00	6.29	0.037	0.260	0.093	2.14	3.43
	Analyzer	70.19	6.61	0.052	0.285	0.060	2.26	3.46
	Difference	-0.81	+0.32	+0.015	+0.025	-0.033	+0.12	+0.03
6	Chemical	68.40	11.47	0.027	0.400	0.060	1.86	1.97
	Analyzer	67.72	11.28	0.032	0.390	0.059	1.94	1.99
	Difference	-0.68	-0.19	+0.005	-0.010	-0.001	+0.12	+0.02
Average Difference		0.44	0.19	0.011	0.048	0.008	0.08	0.06

Measurement time was 10 min.

TABLE 3. Reproducibility of Portland cement rawmix and alumina

Sample	Data	Al2O3	SiO2	SO3	K2O	CaO	TiO2	Fe2O3
Rawmix	Average	2.95	12.05	0.12	0.34	45.21	0.16	2.12
	SD(n-1)	0.025	0.110	0.005	0.008	0.050	0.001	0.006
Alumina	Average	65.07	14.87		1.14	0.30	3.13	1.45
	SD(n-1)	0.150	0.140		0.008	0.007	0.034	0.006

Each specimen was analyzed 21 times. Measurement time for Portland cement rawmix was 12 min and 15 min for alumina.

To overcome partical size and mineral effect, the sample must be ground into flour (pass through 320 mesh sieve) and pelletized at pressure of 600 Kg/cm². 2% wt. grindidng aids was added to improve grinding efficiency.

Above data shows that the precision and accuracy for all elements in the sample including light elements such as Al, Si and neighbouring elements is satisfying to meet the industrial needs

CONCLUSION

The new R.I. source exciting EDXRF analyzer which has been described above can analyze ligh elements such as Al, Si, P, S etc. in air environment without vaccum because of adopting of special made high resolution thin window close proportional gas counter and ring Fe-55 source and carefully geometric distribution designing of source, counter and specimen. The software has sufficient ability of spectrum deconvolution. It overcomes the count rate effect, detects small peak and subtracts background successfully. The analyzer has all advantage of source exciting EDXRF such as simple structure, low cost, good adaptability to environment and easy operating etc.. It extends the applications of source exciting EDXRF analyzer greatly.