Application Note WDXRF1098

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XRF1098 - Fe, Ni and Co alloy analysis by the Fundamental Parameter method using the Simultix 15

Introduction

The multi-channel X-ray fluorescence spectrometer Simultix 15 enables simultaneous measurement of all elements in samples, which makes it ideal for process control in production lines where extremely rapid analysis is required.

Fe, Ni and Co based alloys, including high-temperature alloys, tool steel, and stainless steel, have broad ranges of concentrations for many elements. These alloys are analyzed for production control by X-ray fluorescence (XRF) spectrometry. Numerous calibration curves must be prepared when using the empirical calibration method, even if matrix corrections are introduced, because of strong inter-element absorption and enhancement effects.

The basic theoretical formula of the fluorescent X-ray intensity for the Fundamental Parameter (FP) Method was established by Sherman(1) in 1955. Shiraiwa and Fujino(2) completed the formula by correcting for secondary excitation.

In 1983, Rigaku became the first XRF manufacturer to introduce FP method software for a wavelength dispersive (WD) XRF spectrometer, and the FP method has been widely used in fields from semi-quantitative screening analysis to production control in many industries.

In this note, Fe, Ni and Co alloy analysis by the FP method is demonstrated.

Instrument

The Simultix 15 is a simultaneous wavelength dispersive X-ray fluorescence (WDXRF) spectrometer with multiple-channels, which enables high-throughput analysis. The instrument is designed to provide reliability and stability for routine analysis of production control.

The Simultix 15 is equipped with a 4 kW X-ray tube and fixed channels optimized for the elements to be measured. Configurations with up to 40 fixed channels are available (optional) for simultaneous analysis. High-performance scanning goniometer channels (optional) can also be substituted for some fixed channels. An intelligent Automatic Sample Changer (ASC), capable of placing up to 48 samples, is optionally available for high-demand jobs.

The operation software is improved to facilitate daily-use operation. The newly integrated “Flowbar” in quantitative analysis guides users through the calibration procedure.

Measurement condition

The tube voltage and current applied was 50 kV - 70 mA and all elements were measured simultaneously with a counting time of 20 seconds.

The Lα line was measured for W and Ta and the Kα line was measured for all the other elements.

Table 1 shows the measurement conditions for the analyzing crystals and detectors.

Table 1: Measurement conditions

Analyte	**Mn**	**Si**	**Cr**	**Ni**	**Co**
Crystal	LiF(200)	RX4	LiF(200)		
Detector	S-PC				
Analyte	**Mo**	**W**	**Nb**	**Ti**	**Al**
Crystal	LiF(200)				PET
Detector	SC	S-PC	SC	S-PC	
Analyte	**Fe**	**P**	**S**	**Cu**	**Ta**
Crystal	LiF(200)	Ge	NaCl	LiF(200)	
Detector	S-PC				
Analyte	**V**	**Sn**			
Crystal	LiF(200)				
Detector	S-PC	SC			

Sample preparation

All the samples were polished using 240 grit corundum papers.

Standard and calibration

To make the FP sensitivity calibrations, 118 standard samples were used.

Materials used for standard samples are as follows: Monel, Hastelloy, Waspaloy, Rene41, Nimonic, Haynes, Inconel, Stellite, MP159, 15Mn17Cr, 17-4PH, PH13-8Mo, RA330, Nitr, Maraging, Carpenter20Cb3, tool steel, stainless steel, binary alloy and pure metals of nickel, cobalt and iron.

Table 2 lists the concentration ranges and the accuracies for each element. Accuracies were determined from the standard deviations of the quantified values of the individual samples using the established sensitivity calibrations.

Correlations between standard values and analysis results for representative elements of Cr, Co and Ni are shown in Figures 1 to 3.
In the sensitivity calibrations, overlaps were corrected for P and S by Mo, Co by Fe and Cu by Ni.

Table 2: Accuracy of calibrations (unit: mass%)

Element	Concentration range	Accuracy
Mn	0 - 15.09	0.031
Si	0 - 4.06	0.051
Cr	0 - 39.48	0.10
Ni	0 - 100	0.14
Co	0 - 100	0.071
Mo	0 - 27.9	0.038
W	0 - 17.98	0.065
Nb	0 - 5.38	0.090
Ti	0 - 3.19	0.013
Al	0 - 1.74	0.032
Fe	0 - 100	0.18
P	0 - 0.32	0.002
S	0 - 0.03	0.002
Cu	0 - 32.93	0.020
Ta	0 - 0.75	0.080
V	0 - 2.04	0.012
Sn	0 - 0.09	0.002

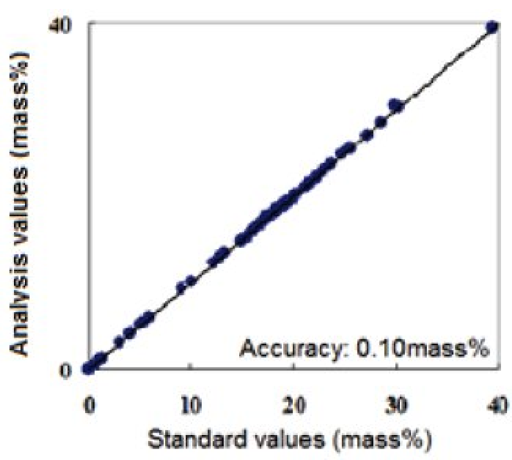

Figure 1: Correlation between standard values and analysis values for Cr.

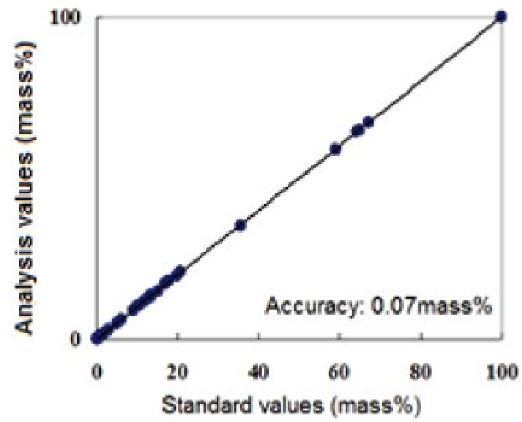

Figure 2: Correlation between standard values and analysis values for Co.

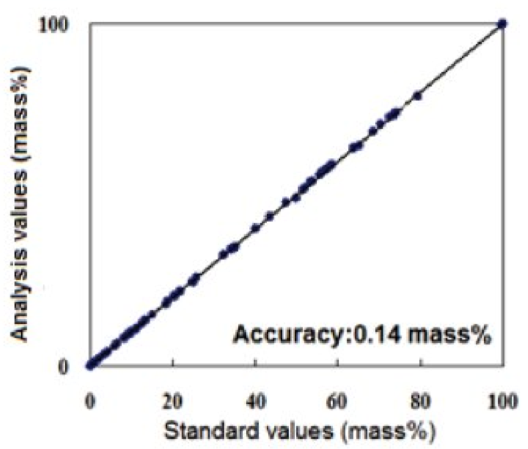

Figure 3: Correlation between standard values and analysis values for Ni.

Analysis results

The repeatability test results are shown in Tables 3 to 5.

Table 3: Repeatability test result of cobalt alloy (unit: mass%)

Element	Average	Standard deviation	RSD%
Si	0.26	0.0007	0.27
Mn	0.79	0.0005	0.06
Ni	1.69	0.0033	0.20
Cr	22.97	0.0062	0.03
W	0.96	0.0021	0.22
Mo	4.70	0.0026	0.06

Fe	0.37	0.0011	0.30
Al	0.41	0.0010	0.24
Co	67.37	0.0073	0.01

Table 4: Repeatability test result of Hastelloy (unit: mass%)

Element	**Average**	**Standard deviation**	**RSD%**
Mn	0.13	0.0003	0.23
Si	0.02	0.0004	2.0
Cu	0.04	0.0007	1.8
Cr	0.11	0.0005	0.45
Mo	27.67	0.0059	0.02
Co	0.05	0.0006	1.2
Nb	0.01	0.0002	2.0
Ta	0.02	0.0013	6.5
W	0.12	0.0012	1.0
Fe	1.00	0.0013	0.13
Al	0.32	0.0015	0.47
Ni	70.45	0.0064	0.01

Table 5: Repeatability test result of tool steel (unit: mass%)

Element	Average	Standard deviation	RSD%
Mn	0.31	0.0003	0.10
P	0.02	0.0003	1.5
S	0.01	0.0002	2.0
Si	0.32	0.0006	0.19
Cu	0.10	0.0005	0.50
Ni	0.30	0.0015	0.50
Cr	4.30	0.0031	0.07
Mo	0.53	0.0010	0.19
W	18.03	0.0058	0.03
Co	4.89	0.0044	0.09
V	1.16	0.0028	0.24
Fe	69.29	0.0052	0.01

Advantages of the Rigaku FP method

The advantages of the Rigaku FP method are as follows:

- The conventional empirical calibration method requires many groups of calibrations and many standards to cover the entire range of these alloys. The FP method can cover entire ranges with only a single group with a minimum number of standards.
- The Rigaku FP program has many unique features such as incorporating tertiary excitation in the theoretical intensity calculation and a theoretical overlap correction for accurate analysis.

Conclusions

The conventional empirical calibration method requires many calibration groups for the analysis of Fe, Ni, and Co alloys. The Rigaku FP method has achieved accurate analysis for the alloys with a single calibration for each element covering very wide ranges of concentrations. The FP method in the Simultix 15 makes sample analysis simple and easy, removing the need for complicated work to classify calibration groups and preparing many standards.

In addition to the FP method, the Rigaku Simultix 15 software can offer all functions required for process control in manufacturing.

References

1) J. Sherman: *Spectrochem. Acta.* **7**, 283 (1955)
2) T. Shiraiwa and N. Fujino : *Jpn. J. Appl. Phys.* **5**, 886 (1966)

Related products

Simultix15

High-throughput tube-above multi-channel simultaneous W
DXRF spectrometer analyzes Be through U.