Application Note WDXRF1071

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XRF1071 - Semi-quantitative FP analysis of geological samples

Introduction

Requirement of quick determination of elements in geological samples has been increasing for industries, environment and earth science. They are, for example, exploration of resource, operation of mining, discrimination of contaminated materials hazardous to environment and human health and characterization for geochemical profiling.

Geological samples are generally composed of wide and various elements. Therefore, the analysis method for such unknown samples requires flexibility in addition to quickness.

Semi-quantitative analysis in modern XRF instruments is a unique method which is performed without any reference materials used for the unknown sample analysis. SQX is Rigaku's semi-quantitative analysis (standardless analysis) program to obtain concentrations by theoretical calculation using the fundamental parameter (FP) method and internal sensitivity library. The calculation is performed by using results of sequential scan measurement from boron or fluorine to uranium. The program is integrated with the theoretical overlapping correction function. Therefore, SQX analysis is highly optimized for screening analysis of unknown geological samples

This note demonstrates determination of the chemical composition in geological samples by using the semi-quantitative analysis method.

Instrument

The ZSX Primus III NEXT and ZSX Primus IV are floor-standing sequential wavelength dispersive X-ray fluorescence (WDXRF) spectrometers, which have advantages in high spectral resolution and high sensitivity from light to heavy elements. The instruments are designed to provide reliable analysis results and their high flexibility provides versatility for a wide range of applications.

These spectrometers are equipped with a Rh target X-ray tube and the maximum tube power is 3 kW and 4 kW, respectively. Up to 10 analyzing crystals can cover from beryllium to uranium.

The instruments also have a built-in intelligent auto sample changer (ASC). The ASC is upgradable to 48 and 96 samples, respectively.

The ZSX Primus III NEXT and ZSX Primus IV are optimized for powder sample analysis by adopting tube-above optics. It minimizes the contamination from sample break during powder sample measurement. The tube-above optics also makes it possible to measure pressed powder samples without any binding agents, especially in semi-quantitative analysis. Pressing without binding agent simplifies sample preparation and reduces labor hours and cost of binding agents.

Operation software provides inexperienced users with easy-to-use operation. The flowbar system fully and supports operation on the setting-up of qualitative and quantitative analysis in particular. The standardless analysis program “SQX” is highly usable to determine quickly which elements and how much of elements are contained in unknown sample without preparation of suitable reference materials.

Sample and sample preparation

A granitic rock (SARM 1 / Mintek) was used as a demonstration sample. The well-dried (2 hours at 105° C) samples were pressed under the pressure of 100 kN using a sample support ring made of aluminum.
The pressed powder method is the most common technique for powder samples in XRF spectrometry. The method does not require any expensive flux and fusion machine, any time-consuming procedure and also any special skill or experience from the operators.

Measurement

The ZSX Primus III NEXT was used for measurement. Sequential scan analysis from fluorine to uranium was performed followed by semi-quantitative analysis (SQX). A fixed angle measurement was also applied for each trace element. The fixed angle measurement is one of unique functions in SQX program. When measurement with this function is performed, the X-ray intensities are counted at fixed angles of a peak top and searched background positions for given time after scanning sequence. It can significantly reduce statistical counting error and improves precision for trace element analysis.

Sequential qualitative scan and semi-quantitative FP calculation are programmed and executed in a successive process.

Results

SQX results and reference values are listed in Table 1. The results by the SQX analysis are in good agreement with the reference values. Table 1 shows both the results obtained by using the standard sensitivity library and by using the “Matching library” function with the standard library. The Matching library is a unique function added to the FP sensitivity library and the function searches a reference sample closest to an unknown sample in concentration and sample property. The results of SQX analysis with the Matching library in Table 1 are drastically improved for light elements. Large errors are often produced in analyzed results of light elements in powder samples owing to grain size and mineralogical effects. In general, geological samples are dominantly composed of light elements due to silicate minerals, so that “Matching library” function is effective to obtain accurate results correcting for the effects in SQX analysis.

Table 1: Analyzed result in granitic rocks (unit : mass%, *: indicative)

Component / Element	Certified value	SQX Value without Matching library	SQX Value with Matching library
SiO_2	75.70	72.8	74.9
TiO_2	0.09	0.099	0.091
Al_2O_3	12.08	13.5	12.6
$T.Fe_2O_3$	2.04	2.1	2.0

MnO	0.021	0.020	0.019
MgO	0.06*	0.046	0.044
CaO	0.78	1.0	0.84
Na_2O	3.36	3.6	3.3
K_2O	4.99	5.8	5.2
P_2O_5	-	0.0075	0.0077
F	0.42	0.68	0.64
Cl	-	0.063	0.061
S	-	0.01	0.0056
Cr	0.0012	0.0016	0.0015
Co	-	0.0001	0.0001
Ni	0.0008*	0.0029	0.0028
Cu	0.0012	0.0024	0.0024
Zn	0.0050	0.0060	0.0061
Ga	0.0027	0.0031	0.0030
As	-	0.0013	0.0013
Rb	0.0325	0.037	0.036
Sr	0.0010	0.0014	0.0013
Y	0.0143	0.013	0.013
Zr	0.0300	0.032	0.032
Nb	0.0053	0.0059	0.0056
Ba	0.0120*	0.0096	0.0090
La	0.0107*	0.013	0.012
Ce	0.0195	0.018	0.017
Nd	0.0072	0.0046	0.0042
Sm	0.00158	0.0010	0.0010
Dy	0.0017*	0.0021	0.0020
Yb	0.00142	0.0018	0.0016
Hf	-	0.0004	0.0004
Pb	0.0040	0.0033	0.0032
Th	0.0051	0.0045	0.0043
U	0.0015*	0.0015	0.0015

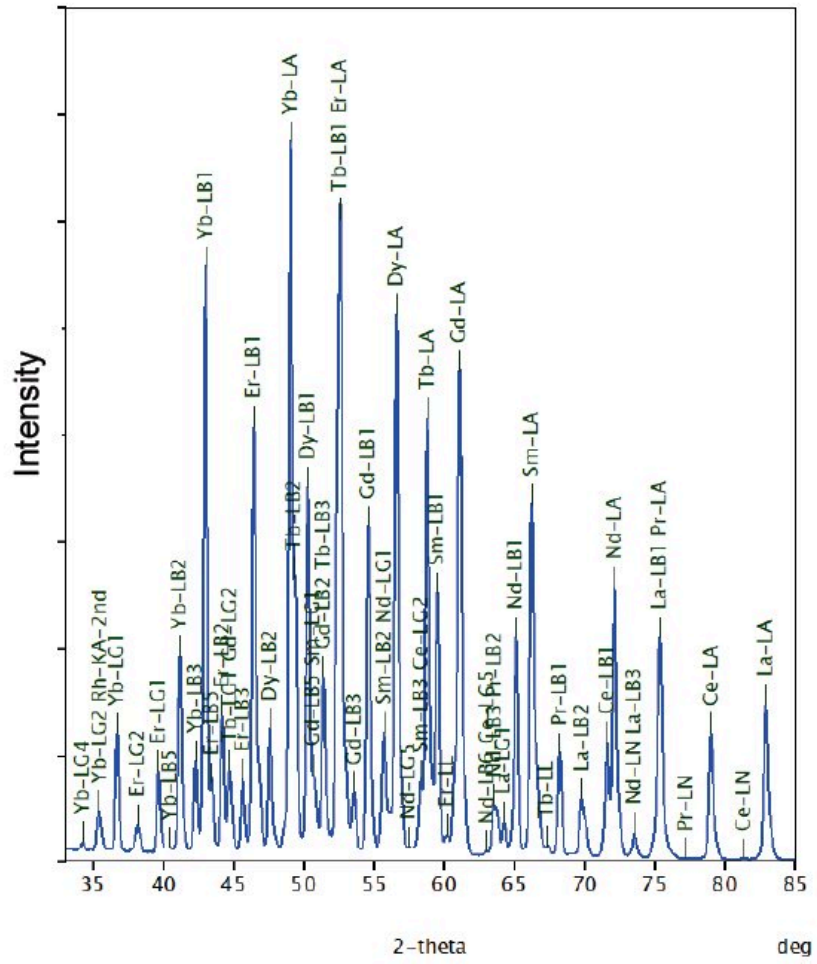

Figure 1: Spectral chart of rare earth elements measured using ZSX Primus III NEXT with the standard optical condition with LiF(200)

In this note, SQX calculation with the Matching library was applied to light elements from calcium to sodium.

The SQX program is also integrated with the theoretical overlapping correction function. Lanthanides in rare earth elements, which are currently of interest as a global issue, are consecutive in atomic number and their spectra (L lines) appear in relatively close range of two-theta angles, so that their spectra are often overlapped with each other (Figure 1). Even in such a complicated spectrum, this function can automatically execute optimized correction without any complicated manual correction operation.

Conclusions

Semi-quantitative analysis by the pressed powder method on WDXRF is powerful technique to quickly obtain chemical compositions of unknown samples. The results above were obtained on the ZSX Primus III NEXT with a 3 kW X-ray tube. The ZSX Primus IV with a 4 kW X-ray tube give better results than ZSX Primus III NEXT in determination for trace elements.

The SQX program has many unique functions effective such as the Matching library for variety of complicated geological unknown samples. The functions improve reliability of the results and versatility for geological sample screening.

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