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# XRF1099 - Trace element analysis in geological samples by the pressed powder method, using GEO-TRACE-PAK

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## Introduction

Trace elements in geological materials, such as rock, sediment, mineral and ore, are important from the stand-point of natural resource and the environment. To establish calibration for trace elements in such a broad range of geological materials, it is necessary to collect many reference materials covering a wide variety of compositions. Furthermore, it is not easy to determine the optimum conditions for trace element analysis of complex matrices of geological materials by the pressed powder method, which is applied because of low concentrations of trace elements.

Rigaku provides an analysis package for trace element analysis of geological materials, named "GEO-TRACE-PAK".

This application note introduces GEO-TRACE-PAK and demonstrates analysis results of trace elements in geological samples using this analysis package.

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## Precalibration package "GEO-TRACE-PAK"

"GEO-TRACE-PAK" is a "pre-"calibration package that provides a quantitative application set including calibration, measuring conditions and analysis parameters. Since the pre-calibration package is pre-installed at our factory, analysis work can start soon after system installation is completed.

"GEO-TRACE-PAK" was developed from over one hundred certified reference materials (geological and ore samples) by the pressed powder method. Using this package, quantitative analysis of 26 trace elements can be carried out. The analysis results of 9 major components are used to correct for the trace element analysis. Two multi-element glass disks included in the package are used for maintenance of the calibration curves.

The contents of GEO-TRACE-PAK are as follows:

- Drift correction samples
  - XRF monitor glass disks, 2 pcs.
- Validation samples
  - Pressed powder disks with binder mixed, 2 pcs.(NIM-GBW07103, NIM-GBW07107)
- Binder for pressing
  - SpectroBlend®, 1 bottle (~200 g)
- Backup CD
  - calibration curves (calibration constants)

- correction coefficients
- measurement conditions
- other application setting
- Instruction manual

The contents of the backup CD are pre-installed on the system before it is shipped. Users do not have to install the package during system installation.

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## Instrument

GEO-TRACE-PAK is applicable to Rigaku's ZSX Primus IV, ZSX Primus IVi and ZSX Primus III NEXT sequential wavelength-dispersive (WD) XRF spectrometer. An optional analyzing crystal LiF(220) is required to add better spectral resolution to the WDXRF spectrometer. In the case of ZSX Primus III NEXT, the optional Ge crystal is also required.

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## Certified reference materials

A total of 101 certified reference materials (CRMs) were used to establish the GEO-TRACE-PAK calibration. The providers of the CRMs used are:

- Geological Survey of Japan
- U.S. Geological Survey
- Canada Centre for Mineral and Energy Technology
- Natural Resources of Canada
- MINTEK (South Africa)
- State Bureau of Technical Supervision, China
- National Research Council Canada
- National Institute of Standards and Technology (U.S.)
- National Research Centre of Geoanalysis (China)
- National Institute for Environmental Studies (Japan)

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## Calibration

Calibration curves for 26 trace elements, as well as 9 major components for reference, were established. The summary of the calibration is shown in Table 1. Theoretical alpha correction, overlap correction and Compton ratio correction were applied when required. Representative calibration curves (Cr, Y and Pb) are shown in Figure 1.

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)

The LLD (lower limit of detection) is calculated by the following formula:

$$LLD = 3 \cdot \frac{1}{m} \cdot \sigma_B = 3 \cdot \frac{1}{m} \cdot \sqrt{\frac{I_B}{1000 \cdot t}}$$

$S_m$ : sensitivity of calibration (kcps/mass%)

$\sigma_B$ : standard deviation of blank intensity (kcps)

$I_B$ : blank intensity (kcps)

$t$ : counting time (s)

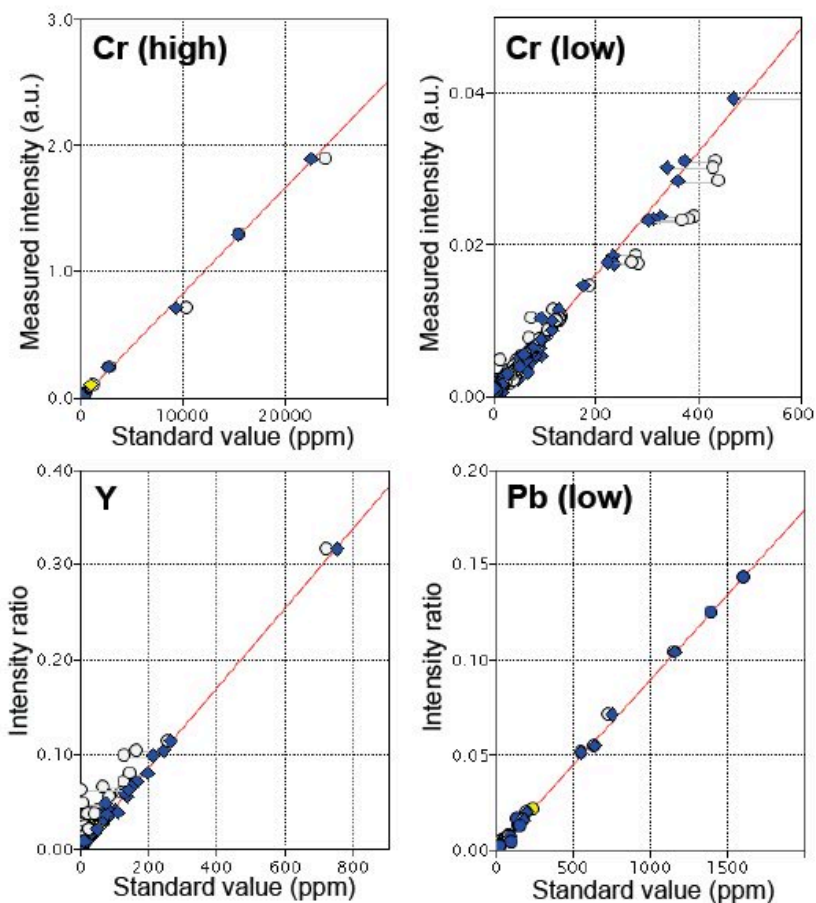
**Table 1:** Calibration summary.

Element	Concentration range (ppm)	Accuracy (ppm)	Correc. <sup>*2</sup>
Sc	3 - 78	4	A, L
V	3 - 768	14	A, L
Cr	3 - 24000	13 / 510 <sup>*1</sup>	A, L
Co	3 - 324	8	A, L
Ni	2 - 3780	5 / 67 <sup>*1</sup>	C
Cu	2 - 37300	11 / 470 <sup>*1</sup>	C
Zn	2 - 27500	12 / 350 <sup>*1</sup>	C, L
Ga	1 - 37	3	C, L
As	4 - 1540	6 / 49 <sup>*1</sup>	C, L
Br	1 - 217	3	C
Rb	1 - 800	7	C, L
Sr	1 - 12000	13 / 21 <sup>*1</sup>	C, L
Y	1 - 718	7	C, L
Zr	1 - 11000	20 / 50 <sup>*1</sup>	C, L
Nb	1 - 3900	3 / 200 <sup>*1</sup>	C, L
Mo	1 - 15100	2 / 23 <sup>*1</sup>	C, L
Sn	1 - 1723	8	C
Ba	7 - 2400	46	A, L
La	5 - 1340	5 / 7 <sup>*1</sup>	A
Ce	4 - 2230	25 / 130	A, L

Nd	4 - 670	4 / 47 <sup>*1</sup>	A, L
W	3 - 3600	35	C, L
Pb	2 - 41700	10 / 580 <sup>*1</sup>	C, L
Bi	2 - 680	36	C, L
Th	2 - 1103	8	C, L
U	2 - 650	3	C, L
<b>Major components (reference)</b>			
<b>Component</b>	<b>Concentration range (mass%)</b>	<b>Accuracy (mass%)</b>	<b>Correc. <sup>*2</sup></b>
CaO	- 55.1	0.9 / 2.7 <sup>*1</sup>	A
TiO <sub>2</sub>	- 7.7	0.06	A
Fe <sub>2</sub> O <sub>3</sub>	- 55.6	1.6	A
Mn	- 1.75	0.019	A, L
K <sub>2</sub> O	- 15.4	0.2	
S	- 7.0	0.3	
P <sub>2</sub> O <sub>5</sub>	- 2.6	0.09	
MgO	- 49.4	1.0	A
Na <sub>2</sub> O	- 10.7	0.3	A

\*1 The calibration curve is split. The values on the left and right are accuracies for the lower and upper parts of the calibration respectively.

\*2 The following corrections are applied: A: theoretical alpha correction; L: overlap correction; C: Compton ratio correction.



**Figure 1:** Representative calibration curve of Cr, Y and Pb. For Cr, the calibration curves for higher and lower ranges are shown. For Y and Pb, Compton scatter ratio correction is applied; the vertical axis of the calibration curve is the intensity ratio of the element line to Rh-K $\alpha$  Compton scatter line.

## Sample preparation

GEO-TRACE-PAK can be applied to pressed powder briquettes either with or without binder. The calibration was established with pressed powder disks of the CRMs without binder, but it includes correction coefficients for the mixing ratio of binder; therefore, the calibration is applicable to variable binder ratios. The binder content should be 20% or less of the total weight. The binder should be SpectroBlend®. Analysis samples should be ground to a grain size of 50  $\mu\text{m}$  or less.

## Evaluation analysis

Analysis for evaluation was performed using the ZSX Primus IV with a 4 kW Rh target X-ray tube. The CRMs, GSR-4 (sandstone) and SY-4 (diorite gneiss) were used for the evaluation analysis; one pressed disk was prepared without binder and another disk was prepared with SpectroBlend® 10% by weight, for each of the CRMs.

The analysis results were tabulated in Table 3.

**Table 2:** Typical lower limit of detection (LLD) (unit: ppm)

Element	LLD	Element	LLD
Sc	1.3	Zr	0.2
V	1.0	Nb	0.2
Cr	1.2	Mo	0.2
Co	0.7	Sn	0.9
Ni	0.8	Ba	4.2
Cu	0.7	La	3.8
Zn	0.6	Ce	5.3
Ga	0.5	Nd	2.6
As	1.2	W	1.1
Br	0.2	Pb	0.7
Rb	0.2	Bi	0.7
Sr	0.3	Th	0.5
Y	0.3	U	0.6

**Table 3:** Evaluation analysis results, using two CRMs, GSR-4 (sandstone) and SY-4 (diorite gneiss). (unit: ppm)

Element	Sample: GSR-4 (sandstone)			Element	Sample: SY-4 (diorite gneiss)		
	Standard value	XRF analysis results			Standard value	XRF analysis results	
		Without binder	10% binder added			Without binder	10% binder added
Sc	4.2	5	6	Sc	1.1	n.d.	n.d.
V	33	39	38	V	8	14	14
Cr	20	26	21	Cr	12	15	13
Co	6.4	6	5	Co	2.8	4	4
Ni	16.6	16	15	Ni	9	6	6
Cu	19	15	16	Cu	7	3	4
Zn	20	20	18	Zn	93	90	88
Ga	5	5	4	Ga	35	33	30
As	9.1	8	9	As	1	1	2

Br	-	n.d.	n.d.	Br	217	221	216
Rb	29	31	31	Rb	55	59	58
Sr	58	60	61	Sr	1191	1171	1170
Y	21.5	22	21	Y	119	124	121
Zr	214	205	201	Zr	517	470	492
Nb	5.9	5	5	Nb	13	9	9
Mo	0.76	n.d.	n.d.	Mo	0.28	n.d.	n.d.
Sn	1.1	1	n.d.	Sn	7.1	10	8
Ba	143	142	145	Ba	340	353	354
La	21	22	24	La	58	62	57
Ce	48	48	50	Ce	122	127	121
Nd	21	20	20	Nd	57	60	61
W	1	n.d.	n.d.	W	3	10	8
Pb	7.6	7	8	Pb	10	10	10
Bi	0.18	n.d.	n.d.	Bi	-	n.d.	n.d.
Th	7	8	8	Th	1.4	1	1
U	2.1	4	4	U	0.8	1	1

n.d.: not detected

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## Conclusions

Rigaku provides the "GEO-TRACE-PAK" precalibration package for trace element analysis in geological materials. The calibration and related parameters, such as measurement conditions and correction coefficients, are pre-installed on the system. Users can start the analysis by running the drift correction samples included in the package.

Since the calibration is established with overlap correction, Compton scatter ratio correction and theoretical alpha corrections by major elements, GEO-TRACE-PAK can be applied for various geological materials.

This package includes correction coefficients for the mixing ratio of the binder, SpectroBlend®. It is possible to choose whether to use the binder or not, or adjust the mixing ratio of the binder depending on the properties of the geological materials to be examined.

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## 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