

Analysis of environmental samples using an energy-dispersive X-ray fluorescence spectrometer NEX CG

Takao Moriyama*

1. Introduction

The elemental analysis of environmental samples is essential for the health of human beings and an accurate and rapid analysis technique is demanded.

ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometry) and AAS (Atomic Absorption Spectrometry) for elemental analysis are typical wet chemistry techniques. On the other hand, X-ray fluorescence (XRF) spectrometry has three advantages: easy sample preparation, high reproducibility and rapid analysis. It has also been widely used for environmental applications.

The energy dispersive X-ray fluorescence spectrometer NEX CG with polarized optics enables data measurements with low background and high peak-to-background ratio (P/B ratio). Therefore, trace amounts of hazardous elements contained in environmental samples can be analyzed with high sensitivity. Moreover, the scattering fundamental parameter method corrects for the influence from non-measurable components in samples such as coal fly ash, soils and biological samples by using Compton and Thomson scattering intensities from a Mo secondary target.

In this paper, the analyses of hazardous and the other elements in a variety of environmental samples such as polluted soil and biological samples are introduced.

2. Instrument

The Rigaku EDXRF (Energy-Dispersive X-ray fluorescence) spectrometer NEX CG used in these measurements and the specifications are shown in Fig. 1 and Table 1.

The NEX CG is equipped with RX9, Cu, Mo and Al

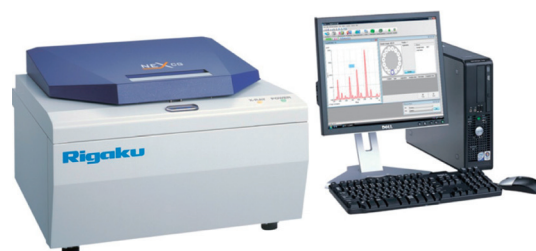


Fig. 1. Rigaku EDXRF spectrometer NEX CG.

Table 1. The specifications of NEX CG.

X-ray tube	Pd target, air cooled
Tube power	50 W: 50 kV–2 mA (max)
Secondary targets	5 targets (max)
Detector	High performance SDD (Silicon Drift Detector)
Atmosphere	Vacuum, Air, He

secondary targets, and the measurement element range is Na~U. A specialized light element optimization (LEO) secondary target is also available for improved analysis accuracies of Na and Mg. A high performance SDD (silicon drift detector), which does not require liquid nitrogen, is utilized for realize high analytical precision and accuracy.

Secondary targets and the polarized optics as shown on the left figure in Fig. 2 provide a high P/B ratio spectrum compared to direct excitation optics in a wide energy range. Blue and red lines on the right figure in Fig. 2 show typical spectra of a multi-element oil sample

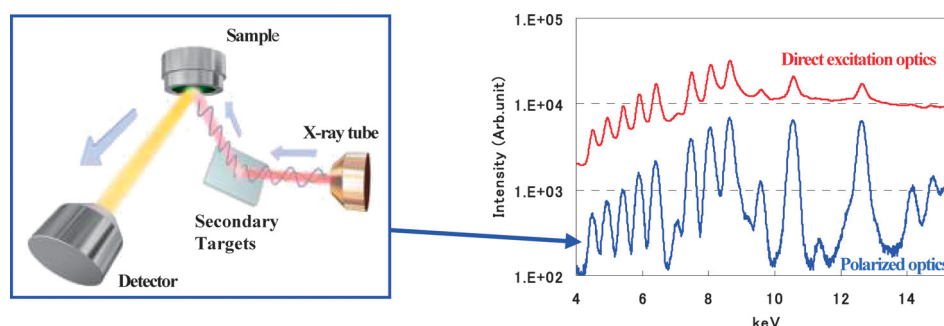


Fig. 2. Polarized optics and comparison spectra with direct excitation optics of an oil sample. (Spectra are rescaled to adjust the intensities at Mo-K α Compton scattered X-rays).

*SBU-WDX, X-ray Analysis Division, Rigaku Corporation.

obtained by the spectrometers with polarized optics and direct excitation optics. Polarized optics gives greatly improved performance compared to the direct excitation optics for trace element analysis.

The biological samples analyzed in this study are generally sensitive to heat. NEX CG has the advantage of causing no radiation damage to the samples because of very low X-ray radiation to sample dose due to indirect radiation in the secondary target optics.

3. Sample Preparation

The biological samples, which were ground and dried, were prepared by hydraulically pressing two grams of the samples at 100 kN into 32 mm diameter pellets by the pressed method using a die.

Soil samples of homogeneous powder <200 mesh (<75 μm particle size) were weighed to three grams and put into polyethylene sample cups of 32 mm diameter using Prolene films (4 μm) for support.

4. Analysis Method

Quantitative analysis by the empirical method requires calibration by several standard samples, which have similar sample matrices to unknown samples. In addition, a high level of analytical skill is required to perform a precise analysis using this method.

Standardless analysis using a FP (fundamental parameter) method is an attractive analysis technique since standards are not required.

The NEX CG includes RPF-SQX (Rigaku Profile Fitting—Spectra Quant X) software for the standardless analysis based on a fundamental parameter method combined with a full profile fitting method⁽¹⁾. The sensitivities are pre-calibrated using pure materials to cover the analyses of all elements from Na to U. The RPF-SQX software can cover unlimited types of samples including multi-layered films and filter paper for water solution analysis.

Rigaku's accurate profile fitting algorithm enables accurate analysis of samples with complex matrices. Figure 3 is an example of this profile fitting technique showing fitted and measured profiles for the standard soil sample JSAC0466. The fitted spectrum is the sum of individually generated profiles using the response function⁽²⁾ and estimated intensities obtained by the FP method for the elements detected. Quantification results are obtained by adjusting the fitted spectrum iteratively until it matches the measured spectrum. As shown in Fig. 3, the calculated spectrum is in good agreement with the measured spectrum. When more accurate analysis results are required, it is also possible to register the sensitivities by using standard samples that are close to the unknown sample in RPF-SQX to improve analytical accuracy. This function is called a “matching library” and was utilized to obtain the results shown below.

In addition, the RPF-SQX features a scattering X-ray FP method⁽³⁾ to estimate the non-measurable components for the analysis of measured components.

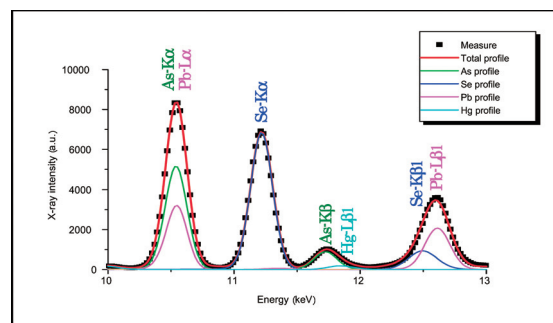


Fig. 3. Measured and fitted spectra of soil standard JSAC0466.

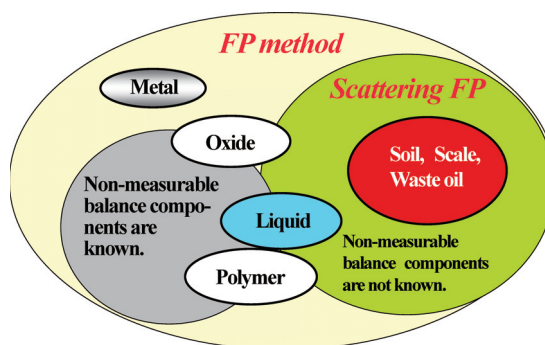


Fig. 4. Applicable samples of scattering FP.

In the conventional FP method, the information of all components in a sample is required for accurate analysis and the composition of non-measurable elements should be known. For example, “CH₂” is set as the balance component for polyethylene or oil samples. However, when the non-measurable elements are not known, accurate results cannot be obtained with the conventional FP method.

The scattering FP method estimates the non-measurable components from the Compton and Thomson scattering X-ray intensities of the Mo-K α line from the Mo secondary target. As shown in Fig. 4, this method gives accurate results for applications of samples containing non-measurable components such as for soil and scale.

5. Results

(a) Analysis of biological samples

Analysis of dietary minerals such as Mg, Ca, K as well as hazardous heavy elements is important in biological samples. Figure 5 shows the spectra of hazardous heavy elements obtained by measuring various kinds of biological standard samples of NRCC CRMs. The peaks of several ppm of hazardous elements could be detected clearly. Figure 6 shows the spectra of mineral elements of Spinach leaves (NIST1570a).

Table 2 shows the analysis results of the biological samples using the RPF-SQX software with the scattering FP method. The influence of high contents of non-measurable elements such as N, O, C and H in these biological samples was effectively corrected.

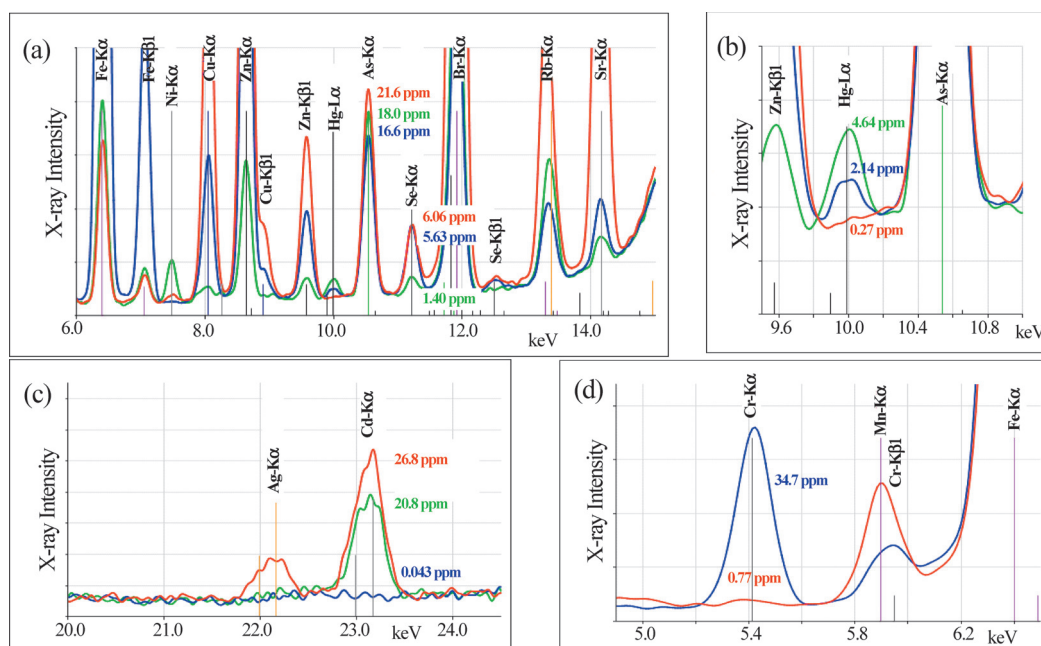


Fig. 5. Spectra of marine organism standard samples from National Research Council Canada. Red lines: Lobster Hepatopancreas (TORT-2), Blue lines: Dogfish Muscle (DORM-2), Green lines: Dogfish Liver (DOLT-2). (a) Mo secondary target, (b) magnified spectrum of (a) in region of Hg, (c) Al secondary target, (d) Cu secondary target.

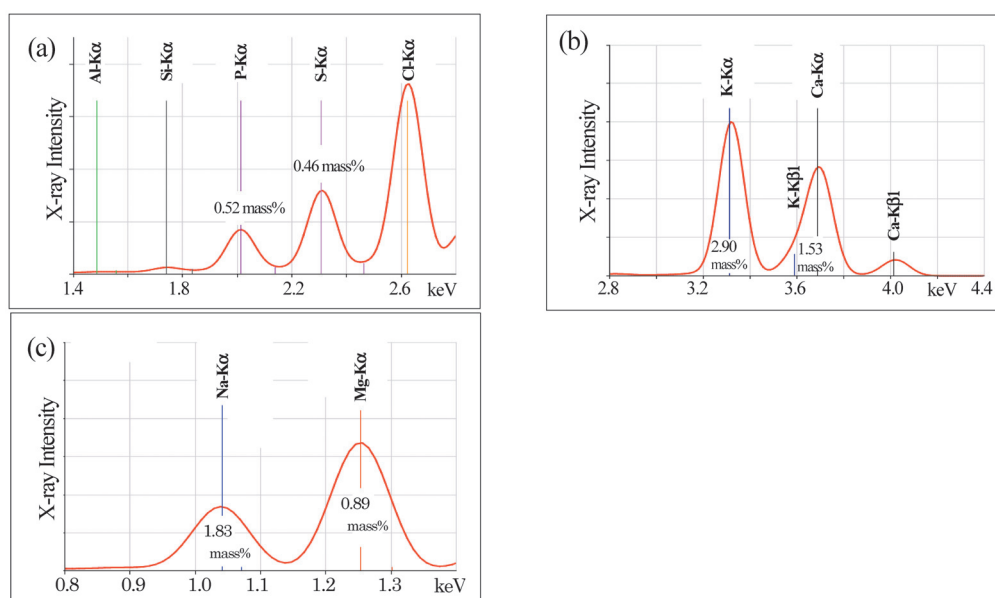


Fig. 6. Spectra of Spinach Leaves (NIST1570a). (a) RX9 secondary target, (b) Cu secondary target, (c) LEO secondary target.

The advantage of the LEO secondary target is shown in Fig. 7. This figure compares the spectra of Na and Mg measured by the LEO secondly target and the RX9 target for the sample of NIST1549 (Non-fat milk powder sample). This standard sample contains 4970 ppm of Na and 1200 ppm of Mg. It also contains 1.06 mass% of P, 0.351 mass% of S and 1.09 mass% of Cl.

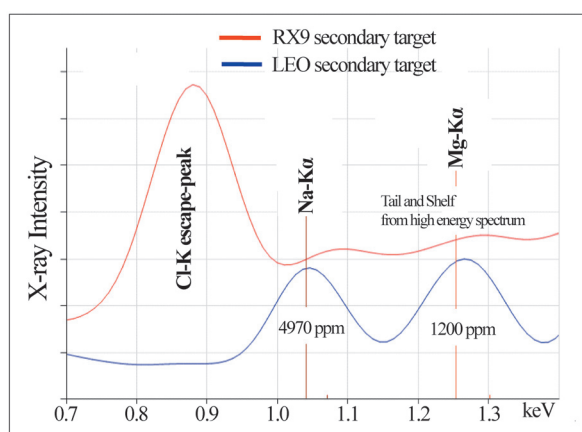
The Pd-L α monochromatic X-rays from the RX9 secondary target have excellent excitation efficiency

for P, S and Cl. In this example, high fluorescent X-ray intensities of P, S and Cl are detected and it causes a large increase of background in low energy side such as the range of Mg and Na lines due to the tail and shelf of the P, S and Cl peaks. Additional sum peak and escape are also generated. The red line in Fig. 7 is the spectrum measured with the RX9 secondary target. The escape peak of Cl-K α appears at 0.88 keV. The background is also higher entirely due to the influence of tail and shelf of P, S and Cl. Therefore, it is difficult to analyze trace

Table 2. Analysis results of various biological samples.

Samples		Na	Mg	Si	P	S	Cl	K	Ca	Mn	Fe	Co
		mass%	mass%	mass%	mass%	mass%	mass%	mass%	mass%	ppm	ppm	ppm
Spinach leaves	Analyzed	1.83	0.85	0.11	0.59	0.50	0.65	2.79	1.47	66.5	271	n.d.
(NIST1570a)	Certified	1.82	0.89	—	0.52	0.46	—	2.90	1.53	—	—	—
Pepperbush	Analyzed	n.d.	0.38	0.27	0.14	0.26	0.39	1.58	1.45	2021	215	15.6
(NIES CRM No.1)	Certified	—	0.41	—	0.11	—	—	1.51	1.38	2030	205	23.0
Dogfish lever	Analyzed	0.83	0.12	n.d.	1.08	1.29	0.83	0.87	0.06	5.7	1124	n.d.
(NRCC DOLT-2)	Certified	—	—	—	—	—	—	—	—	6.9	1103	—
Samples		Ni	Cu	Zn	As	Se	Br	Rb	Sr	Cd	Ba	Hg
		ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Spinach leaves	Analyzed	2.2	14.0	80.0	n.d.	n.d.	34.5	13.0	52.7	n.d.	n.d.	n.d.
(NIST1570a)	Certified	2.1	12.2	82.0	—	—	—	13.0	55.6	—	—	—
Pepperbush	Analyzed	10.3	12.9	347.5	n.d.	n.d.	0.8	75.5	35.0	5.7	165.5	n.d.
(NIES CRM No.1)	Certified	8.7	12.0	340.0	—	—	—	75.0	36.0	6.7	165.0	—
Dogfish lever	Analyzed	—	27.7	90.8	14.2	5.7	23.7	2.0	2.7	21.1	—	1.6
(NRCC DOLT-2)	Certified	—	25.8	85.8	16.6	6.1	—	—	—	20.8	—	2.1

n.d.: not detected

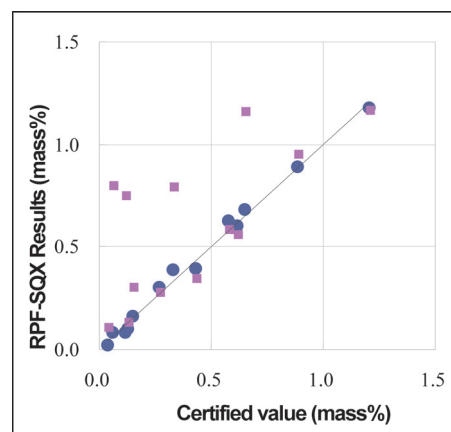
**Fig. 7.** Comparison of spectra using RX9 secondary target and light element optimization (LEO) secondary target of Non-fat Milk Powder (NIST1549).

Na and Mg.

On the other hand, the LEO secondary target excites Na and Mg effectively and does not excite P, S and Cl. The blue line in Fig. 7 is the spectrum measured with the LEO secondary target. Compared to the RX9 secondary target, the peaks of Na-K α and Mg-K α could be clearly detected with an excellent P/B ratio.

In order to confirm the further advantage of the LEO secondary target, Mg in plant and animal standard samples was analyzed using the RX9 and LEO secondary targets. Figure 8 shows the correlation of the certified values and the analysis results for each target. As shown in the figure, accurate results could be obtained in the LEO secondary target.

Due to the LEO secondary target, the accurate

**Fig. 8.** Correlation of standard values and the analysis results at each target of various biological samples.

●: LEO secondary target, accuracy=0.031 mass%
 ■: RX9 secondary target, accuracy=0.29 mass%

analysis of Mg has been realized although it is typically considered difficult to do with general EDX systems. Similarly, good improvement can be expected for Na analysis as well.

(b) Analysis of coal fly ash and soil samples

The hazardous element analysis of fly ash and soil is currently a popular topic in XRF analysis. Samples of coal fly ash and soil were measured using the loose powder method. Figure 9 shows the spectra of the samples of fly ash and soil samples of NIST CRMs. It shows the energy range for As, Se and Pb and the peaks of the trace elements are clearly detected. Table 3 and Table 4 list the analyzed results of hazardous elements

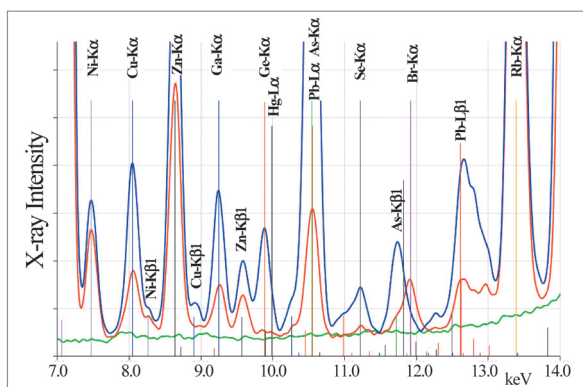
Table 3. Analysis results of trace hazardous elements for fly ash and soil.

Samples		As	Cd	Cr	Hg	Pb	Se
		ppm	ppm	ppm	ppm	ppm	ppm
San Joaquin soil	Analyzed	17.9	n.d.	120.6	3.9	21.2	2.3
(NIST2709)	Certified	17.7	0.4	130.0	1.4	18.9	1.6
Coal fly ash	Analyzed	149	n.d.	189	n.d.	75.8	12.6
(NIST1633a)	Certified	145	1.0	196	0.16	72.4	10.3

n.d.: not detected

Table 4. Analysis results of major elements for fly ash and soil.

Samples		Na	Mg	Al	Si	P	S	K	Ca	Ti	Fe
		mass%	mass%	mass%	mass%	mass%	mass%	mass%	mass%	mass%	mass%
San Joaquin soil	Analyzed	1.35	1.84	7.93	29.26	0.063	0.090	1.95	2.02	0.34	3.51
(NIST2709)	Certified	1.16	1.51	7.50	29.66	0.062	0.089	2.03	1.89	0.34	3.50
Coal fly ash	Analyzed	0.31	0.405	14.4	23.3	0.23	0.19	1.91	1.06	0.31	9.0
(NIST1633a)	Certified	0.17	0.455	14.3	22.8	—	—	1.88	1.11	—	9.4


Fig. 9. Measured spectra of coal fly ash (NIST1633a: blue line) and San Joaquin soil (NIST2709: red line) in the range of 7 to 14 keV using Mo secondary target.

and major elements, respectively. RPF-SQX with the scattering FP method was applied to the analysis of both samples. The analyzed results matched well with the certified values even though the fly ash sample contains unburned carbon and the soil sample contains organic matter.

6. Conclusion

Rigaku's NEX CG, an EDXRF spectrometer with secondary targets, polarized optics, and high-speed detector demonstrated extremely high P/B ratios from light to heavy elements resulting in low LLD results. Accurate analyses down to the ppm level could be achieved even in complex sample composition using quantification software that combined the fundamental parameter method and full profile fitting. The scattering FP method is able to correct for non-measurable components in samples such as soils, biological samples by using Compton and Thomson scattering intensities from a Mo secondary target.

References

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