Wavelength dispersive X-ray fluorescence spectrometer

ZSX Primus IVi

1. Introduction

X-ray fluorescence (XRF) spectrometry is one instrumental analysis method used to determine the composition of solid and liquid samples. Compared to other methods, it can achieve high-precision analysis. XRF is widely used for quality control in manufacturing. It is an effective method for trouble analysis during production and research and development of materials and products.

Rigaku's ZSX Primus series of sequential wavelength dispersive X-ray fluorescence spectrometers includes tube-above high-end ZSX Primus IV, basic ZSX Primus III+, and high-end tube-below ZSX Primus. The different instruments in this series are optimal for coping with a variety of analysis purposes. There are noteworthy advantages to both tube-above and tube-below optics.

Advantages of tube-above optics: With this configuration, there is less concern about contaminating the sample chamber by scattering or spilling powder. There is no need for binders when making briquettes, thus avoiding problems due to sample heterogeneity. High-precision analysis can be performed without decreasing sensitivity due to sample film and film impurities.

Advantages of tube-below optics: This geometry is suitable for analysis of samples such as liquids, alloys, and coated plates. Liquid samples can be easily measured by pouring them into sample cells with sample film attached. Bulk samples such as disc-shaped alloys, coated plates, and glass plates can be measured by placing them on a sample holder with the measurement surface facing down. Samples that are difficult to make into briquettes, such as granular samples, low amount samples, or small fragments, can be placed as they are on the film attached to the sample cells. This makes it easy to perform measurements on rare samples, minimizing sample preparation.

The ZSX Primus IVi, a successor to the tube-below ZSX Primus, is newly developed based on the latest technology cultivated in the ZSX Primus IV.

With the hardware and software platforms unified between ZSX Primus IV and ZSX Primus IVi, it is now possible to share applications between both models.

The main features of the ZSX Primus IVi are as follows:

(1) Qualitative/quantitative application conditions and parameters can easily be transferred between user sites.
(2) Easy management of automatic instrument calibration.
(3) Standardless FP analysis has been improved, and various intelligent functions make it possible to obtain more accurate analysis results more conveniently.
(4) "Automatic Quant Application Setup" allows beginners to perform analysis with high reliability.
(5) High-throughput with high-accuracy/high-sensitivity analysis and reduction of measurement overhead time.

(1) to (4) are due to newly developed functionalities in the ZSX Guidance software, which has both operability and intelligence. (5) is due to the counting system, which employs a 1024-channel D-MCA (Digital Multi Channel Analyzer), which was adopted in ZSX Primus IV. High accuracy is achieved by fully utilizing the data obtained with the D-MCA. In addition, high-sensitivity analyzing crystals can be installed to improve sensitivity, and the overhead of measurement

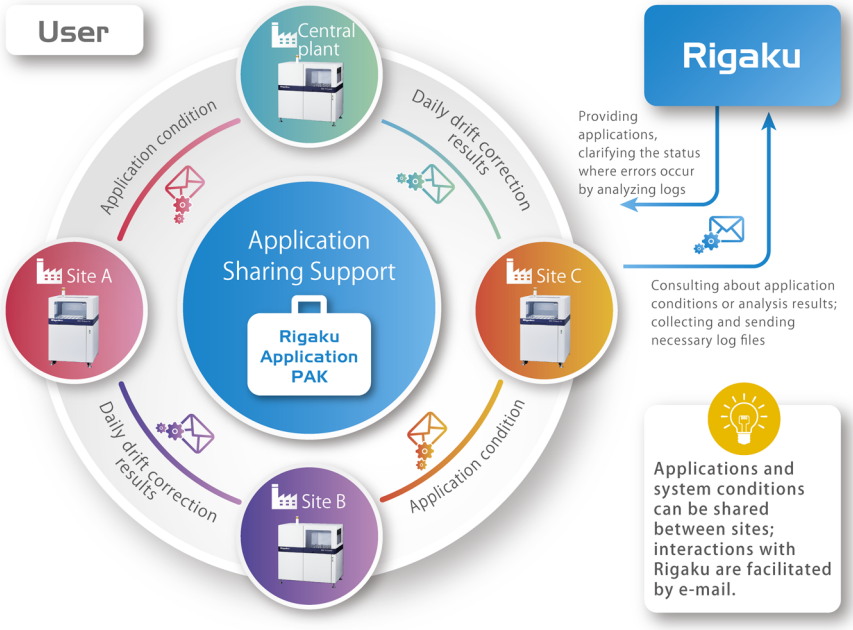


Fig. 1. Conceptual diagram of Rigaku's application sharing support.

time has been significantly reduced by revising the sample transfer and measurement sequence, enabling high-throughput analysis. These features can improve analysis efficiency.

In this article, some of (1), (2) and (3) are explained.

2. Application Sharing Support

To improve production efficiency, production plants are being moved from the home site to other remote sites at an accelerating pace. This increases the need for rapid transfer of analysis applications being used and newly established applications. It is also becoming important to conveniently acquire the operating status of applications at remote sites.

To address this situation, ZSX Primus IV and ZSX Primus IVi use a common platform for hardware and software. This facilitates application sharing between users or between Rigaku and users (Fig. 1).

2.1. Application condition (quantitative/qualitative) import/export software

Transfer of the operating application conditions to another instrument was a burden for users because dedicated staff had to work to establish applications according to the destination instrument. Faster analysis condition setup and an easier transferring procedure were demanded. To fulfill this demand, the application condition import/export program was developed.

When quantitative application conditions are transferred, the system configuration (primary X-ray filters, crystals, detectors and diaphragms) of the source instrument is compared to that of the destination instrument. When the configuration is different between the two instruments, transfer is carried out using alternative conditions optimized for the destination instrument.

For example, in the case of analyzing crystals composed of synthetic multilayers, the lattice spacing (2d value) of crystals of the same type varies depending on the individual crystals, and even the 2-theta angles for the same element line can vary slightly. In this case, the peak angles of the analyzing crystal of the destination instrument and the background angles are automatically fixed according to the differences in lattice spacing.

When the destination instrument does not have the same crystal used in the source instrument, the software searches for an alternative crystal. When transfer conditions are satisfied, an alternative crystal is assigned, and peak and background angles are fixed to those of the alternative crystal of the destination instrument.

When a special compound is used as an analyzing component of an application in the source instrument and that compound has not been registered in the destination instrument, additional registration of the compound is automatically carried out.

Also, when other components in the configurations are different between instruments, alternative conditions are automatically assigned during transfer, taking account of the characteristics of those components.

The information from the quantitative application conditions to be transferred and not to be transferred are as follows:

〈Parameters and data to be transferred〉

Application names, analysis components, types of analyses, sample preparation information, standard sample information, analytical parameters, drift correction sample data, degrees of calibration equation, matrix correction coefficients, overlap correction coefficients, limit range conditions, check analysis conditions and bias correction sample data

〈**Parameters and data not to be transferred**〉
Calibration coefficients

After the transfer, it is possible to directly re-measure the standard samples by preparing the standards registered by the destination instrument. The software automatically recreates calibration curves using the recalibration function. Accordingly, the troublesome re-setting of various parameters is unnecessary.

The setup of standardless FP analysis (SQX analysis) is often used in qualitative application conditions. For the ZSX Primus IV and ZSX Primus IVi, it is also possible to transfer qualitative application conditions easily between instruments.

The outline of the actual application transfer procedure is described below.

Using the data pack program, select the specific application that contains the user setting data, including instrument-dependent information on the data type, the analysis conditions, and the application file (Fig. 2). Required files are automatically compressed into a single file.

It is easy to send the compressed file to the remote site by e-mail because only the minimum required files are selected and compressed. Save this compressed file to a folder on the PC of the transfer destination instrument. Select 〈Import applications created with other ZSX〉 and 〈Use data pack file created with export〉 from the application settings of the destination ZSX Guidance software, and specify the folder containing the compressed source file. The transfer will be done automatically after specifying the application name.

The application conditions can be shared not only between ZSX Primus IVi instruments but also between ZSX Primus IV and ZSX Primus IVi.

3. Automatic Instrument Calibration

To control instrumental drift during routine quantitative analysis, it is recommended to analyze a check sample for each application before drift correction. If the analysis result of the check sample is out of tolerance, drift correction should be performed. Then the check sample is analyzed again and, after confirming that correct analysis values are obtained, daily analyses can be started. Previously, this preparatory work for each application was performed by the analyst following a prescribed procedure before performing daily analyses. There was a demand for an efficient calibration method and subsequent analysis value check.

To automate these preparatory works, options for daily, weekly, monthly, day of the week, and start time have been newly added to the Program Operation function. Thus, unattended calibration has become realized (Auto drift correction function). Preparation for analysis can be greatly reduced with this function. Here is an example sequence for drift correction using the Auto drift correction function.

(1) The system automatically starts up according to the specified schedule (daily/weekly/monthly and start time).
(2) The check sample is analyzed.
(3) Automatically check whether the analysis values of the check sample are within tolerance.
(4) If the result is out of tolerance, drift correction coefficient update is executed automatically by measuring drift correction samples.

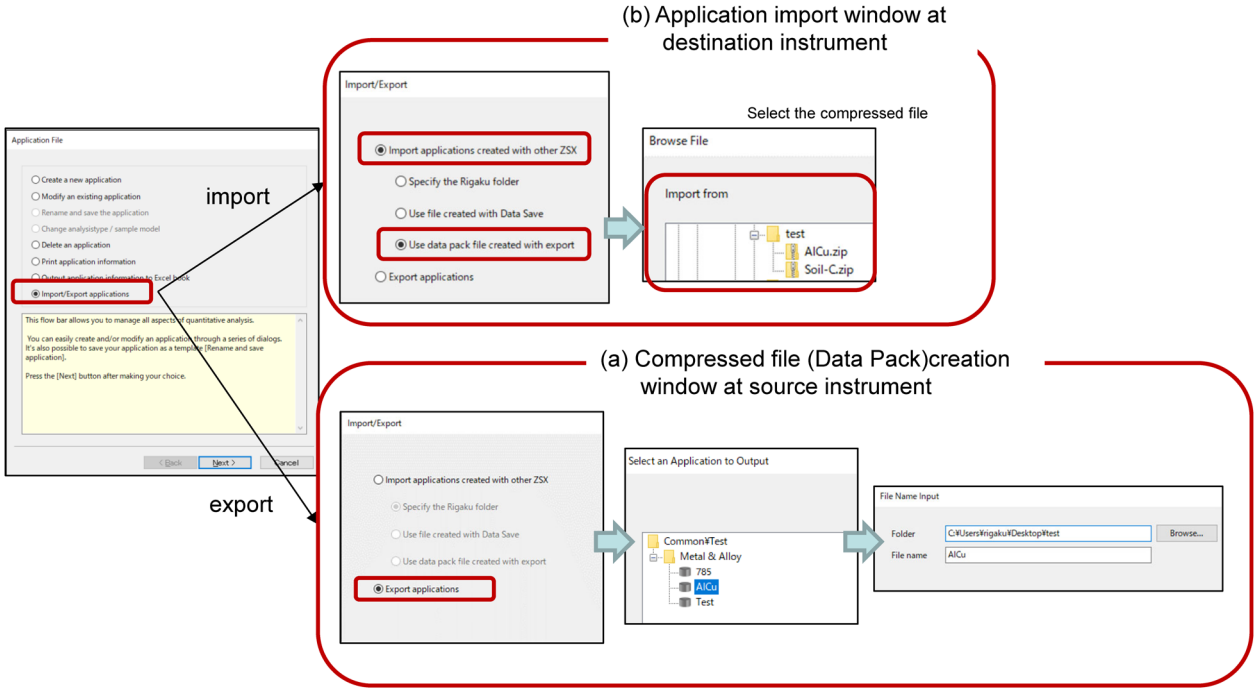


Fig. 2. Application import/export software.

(5) Analyze the check sample again and confirm the analysis result.

The only settings that need to be made in the analysis software are only to register the check sample analysis and drift correction settings in the sample ID table dedicated to automatic drift correction coefficient update, select the sample ID table in Program Operation, and set the schedule (Fig. 3).

4. Further Advances of SQX Analysis

SQX analysis is a standardless FP analysis. It does not need any standard samples, and it uses qualitative analysis results. SQX analysis has advanced, adding excellent easy-to-use and self-evaluation functions. The new features are listed below.

(a) Evaluates the influence of higher-order lines derived from mainly heavy elements, automatically selects the optimum measurement conditions, thereby realizing more accurate SQX analysis.
(b) Fixed-angle measurement setting mode to detect trace elements has been added to EZ scan.
(c) Super-fast mode, whose total measurement time is within 2 minutes, has been added to EZ scan.
(d) Screening for multilayer film samples has been realized.
(e) Any type of sample films can be added to the Sample Film Correction.
(f) SQX scattering FP analysis is available more easily and widely.
The scattered X-ray intensities obtained by the standard analyzing crystal LiF (200) can be used.
SQX scattering FP analysis can be applied to the re-calculation of SQX analysis results.
Measurement diameter of 30 mm is newly supported, as well as 20 mm.
In this article, details of (a) and (f) in SQX analysis are described below.

4.1. SQX analysis considering the influence of higher-order lines

Since wavelength dispersive X-ray fluorescence spectrometers have excellent spectral resolution, peak identification analysis can be performed accurately. However, higher-order lines can interfere with the analysis line.

When a higher-order line interferes with an analysis line, this new function automatically selects data obtained with the optimum measurement condition based on the results of peak identification. Using the spectrum least affected by the higher-order line,

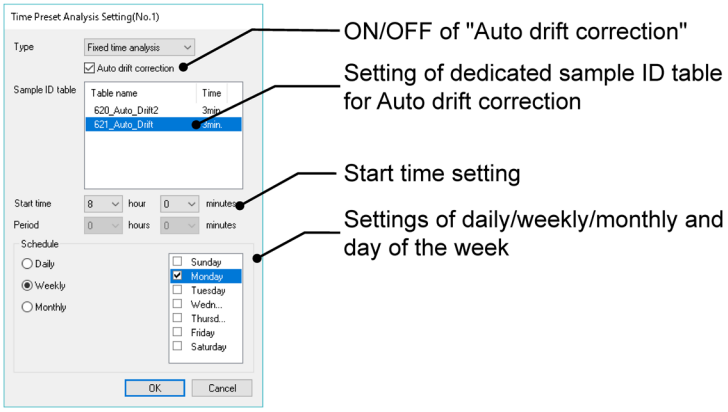


Fig. 3. Auto drift correction setting window in the programmed operation.

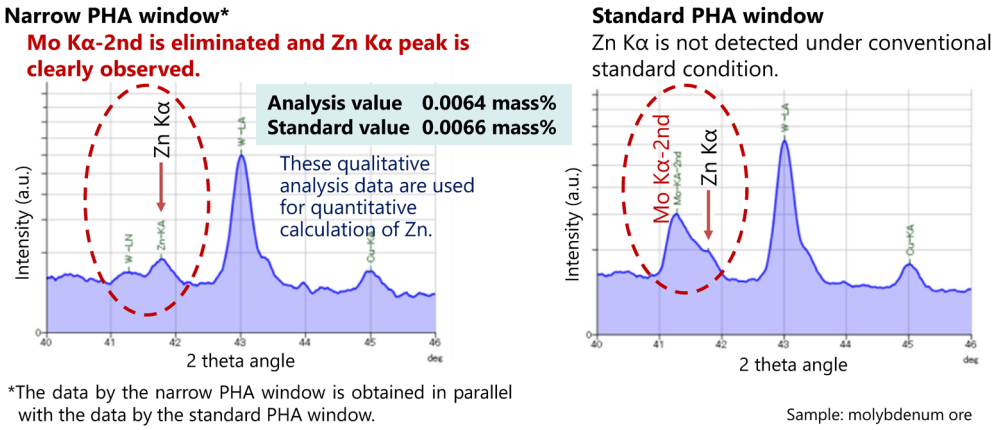


Fig. 4. Zn Kα spectral charts of molybdenum ore powder.

Table 1. SQX analysis results of a molybdenum ore.
Unit: mass%

Component	Analysis value	Standard value	Component	Analysis value	Standard value
Na	0.073	0.056	Ni	0.0034	0.0018
Mg	0.734	0.519	Cu	0.0114	0.0094
Al	1.52	1.83	**Zn**	**0.0064**	**0.0066**
S	2	1.64	Ga	0.0027	0.0025
K	0.038	0.0382	Y	0.0017	0.0011
Ca	23	22.3	Mo	1.66	1.51
Ti	0.075	0.078	Sn	0.011	0.0087
Mn	1.14	0.835	W	0.35	0.36
Fe	14.5	14.9			

quantification calculation is performed by the FP method. This allows even inexperienced operators to obtain accurate analysis results.

An example of SQX analysis of molybdenum ore powder is described in Fig. 4. It shows the spectral chart of Zn Kα, and Table 1 shows the SQX analysis results. Conventionally (with standard PHA window settings), a trace amount of Zn is not detected because the Zn Kα peak is hidden by the large peak of Mo Kα-2nd. With the new function, data with a narrow PHA window setting are acquired at the same time as those for the standard PHA window setting, and Zn Kα peak can be detected under the narrow PHA window setting condition in which the influence of the higher-order Mo line was eliminated. Narrow PHA setting data was automatically selected for the Zn Kα line, and an analysis value of 0.0064 mass% was obtained, which was in good agreement with the standard value of 0.0066 mass%.

4.2. Analytical function utilizing scattering X-rays (SQX scattering FP method)

For measurement with a tube-below X-ray fluorescence spectrometer, the sample is often supported with a polymer film to prevent it from dropping. Owing to absorption by the film, fluorine and lighter elements cannot be detected. In such a case, the influence of ultra-light elements (C, H, N, O, etc.), which are non-measured components, is estimated using scattering X-rays. Accurate SQX analyses of samples containing non-measured components, such as sludge and scale, are possible by considering the influence of non-measured components. Figure 5 shows the applicable range of the SQX scattering FP method.

Since the new SQX scattering FP method supports standard measurement condition data (analyzing crystal LiF(200)), the dedicated measurement conditions for scattered X-rays using analyzing crystal LiF(220) are no longer necessary and standard SQX analysis data can be recalculated by the SQX scattering FP method.

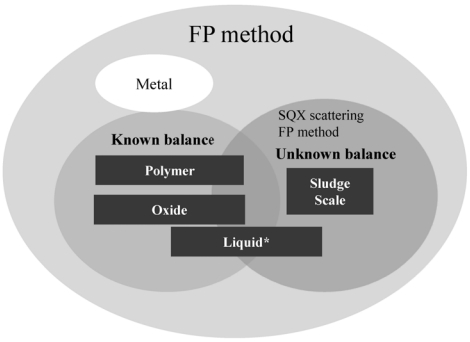
Standardless FP analyses of twenty-four samples (animals/plants/food) were performed using the SQX scattering FP method. The ZSX Primus IVi was used for the measurements. The measurement samples were pressed into briquettes and the measurement surfaces were covered by 6 μm thick polypropylene films. In the quantitative calculation, the sample size information of weight/area/height was set and the influence of the sample thickness was corrected. Table 2 lists the measured samples. It was estimated that the samples have a variety of balance components.

Figures 6(a) and 6(b) show the correlation diagrams between the XRF analysis values and standard values for each light element from Na to Ca. In the SQX scattering FP method, the appropriate balance component is automatically set, and a good correlation

Table 2. Samples analyzed by the SQX scattering FP method.

Type	*Provider	Code	Sample name
Animal	NIST	NIST SRM1755b	bovine liver powder
Animal	NRCC	TORT2	lobster hepatopancreas powder
Fish	NRCC	DOLT2	dogfish liver powder
Fish	NRCC	DORM2	fish muscle powder
Plant	NIST	NIST SRM1570a	spinach leaves
Plant	NIST	NIST SRM1573a	tomato leaves powder
Plant	NIST	NIST SRM1515	apple leaves powder
Plant	NIST	NIST SRM1572	citrus leaves powder
Plant	NIST	NIST SRM8412	corn stalk powder
Plant	BCR	BCR-CRM100	beech leaves powder
Plant	BCR	BCR-CRM101	spruce needles powder
Plant	BCR	BCR-CRM062	olive leaves powder
Plant	BCR	BCR129	hay powder
Plant	NRCG	GBW07603	bush branches and leaves
Plant	NRCG	GBW08501	peach leaves
Plant	BCR	BCR-CRM482	lichen powder
Plant	BCR	BCR-CRM281	rye grass powder
Plant	NRCG	GBW7604	poplar leaves powder
Plant	NIES	NIESNo-7	tea leaf
Food	NIST	NIST SRM1567a	wheat flour powder
Algae	NIES	NIESNo-3	algae
Food	NIST	NIST SRM1549	non-fat milk powder
Food	NMIJ	NMIJ7405a	seaweed hijiki
Food	BCR	BCR-CRM151	milk powder

*Supplier names
National Institute of Standards and Technology (NIST)
National Research Council of Canada (NRCC)
Community Bureau of Reference (BCR)
National Research Centre of Geoanalysis (NRCG)
University of Tokyo Institute of Environmental Studies (NIES)
National Metrology Institute of Japan (NMIJ)



*For liquid, SQX Scattering FP is available only with ZSX Primus IVi .

Fig. 5. Applications of SQX scattering FP method.

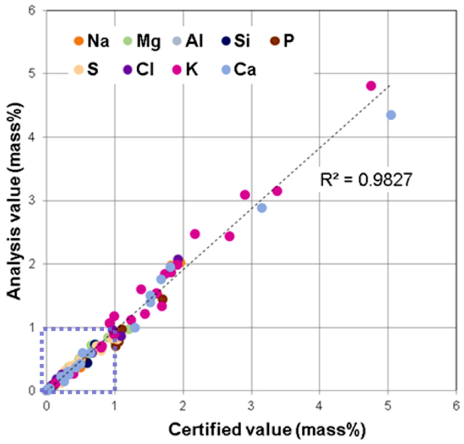


Fig. 6(a). The SQX scattering FP analysis results of animal/plant/food(Up to 6 mass%).

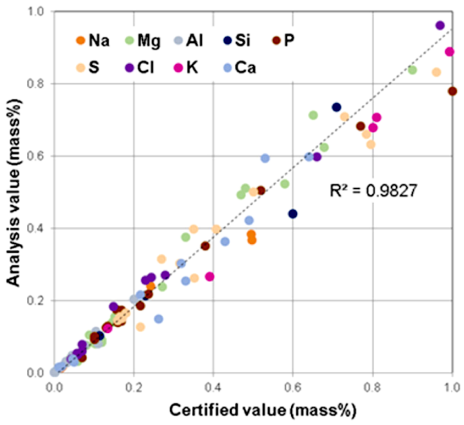


Fig. 6(b). The SQX scattering FP analysis results of animal/plant/food (enlarged view, up to 1 mass%).

coefficient of 0.98 was obtained between the XRF analysis value and the standard value.

Especially in the light element region, it tends to be difficult to obtain accurate balance component information of a totally unknown sample, and the influence of coexisting elements greatly varies depending on the setting of the non-measured components of oxygen (O) and lighter elements. If the balance setting input is not appropriate, the analysis value will deviate significantly from the true value, and the reliability of the analysis value will be impaired.

By the SQX scattering FP method, the influence of non-measured components can be automatically corrected. Errors due to settings made by the analyst are eliminated and the reliability of the analysis values is improved.

Fig. 7. The sample tray system.

Fig. 8. ASC drawer.

5. Sample Handling Suitable for Routine Analysis

The tube-below ZSX Primus IVi uses a sample tray system (Fig. 7) for the sample changer. The sample loading system with trays can improve the efficiency of routine analysis. You can also pull out the ASC drawer of the sample changer (Fig. 8) and, since the ASC drawer is designed low, you can easily exchange samples without getting up from your chair.

6. Summary

The newly developed tube-below sequential wavelength-dispersive X-ray fluorescence spectrometer ZSX Primus IVi is optimal for various analytical applications by adopting new operation software that combines both ease of use and expertise and the latest hardware elements. It can be widely used for research and development as well as process control analyses.