Rigaku

# Application Note

XRF 1092

# Fixed Angle Measurement using the Semi-Quantitative Analysis Function "SQX" of ZSX Guidance Software

**Application**

polymer
non-routine samples

**Instrument**

Wavelength dispersive
X-ray fluorescence spectrometer
**ZSX Primus IV, ZSX PrimusIII+**
**ZSX Primus 400, Supermini200**
**(ZSX Primus)**

**ZSX Primus IV**

**Keywords**

semi-quantitative analysis
standardless analysis
fixed angle measurement
trace elements

## Introduction

X-ray fluorescence (XRF) analysis has been widely used for quality control or production control in a variety of industries because it has many positive features, such as simple sample preparation, short analysis time, and high repeatability with low human error, compared to other elemental analysis methods, such as ICP-OES or AA.

Current XRF spectrometers are also capable of analyzing non-routine samples, such as for screening, material identification or investigating newly developed materials in R&D, owing to the semi-quantitative (or standardless) analysis function using the fundamental parameter (FP) technology. Progress in the FP method has improved the accuracy of semi-quantitative analysis in XRF.

The ZSX Primus family of sequential wavelength dispersive (WD) XRF spectrometers and the bench-top WDXRF spectrometer Supermini200 all have the semi-quantitative analysis program "SQX", a scanning-based program. One feature of SQX is a "fixed angle measurement" function. The combination of scanning and fixed angle measurements improves precision in semi-quantitative analysis.

This application note demonstrates the fixed angle measurement function in SQX by taking a trace of Ti and V in a polymer as example.

## Instrument

The ZSX Primus IV, a tube-above sequential WDXRF spectrometer, is equipped with a 4 kW X-ray tube with a Rh target featuring an ultra-thin beryllium window, and four analyzing crystals covering $_{8}$O to $_{96}$Cm.

## Sample

Three polyethylene samples were used for this demonstration. Samples in pellet form were hot-pressed at 170°C to form disks.

## Measurement

SQX analysis was carried out. In SQX analysis, a qualitative scan is run, and the detected elements are then quantified by the fundamental parameter (FP) method without the use of reference standard samples. In the quantifying process, a sensitivity library is used that has the FP sensitivities for all elements that can be analyzed by XRF. The sensitivity library has been calibrated using pure metals and reagents.

In this application note, the "fixed angle measurement" function was applied to Ti and V. Using this function, X-ray intensities are collected at fixed two-theta angles for a user-specified time, usually much longer than for each step in scanning mode; therefore, precision is improved and superior results can be obtained for trace element analysis.

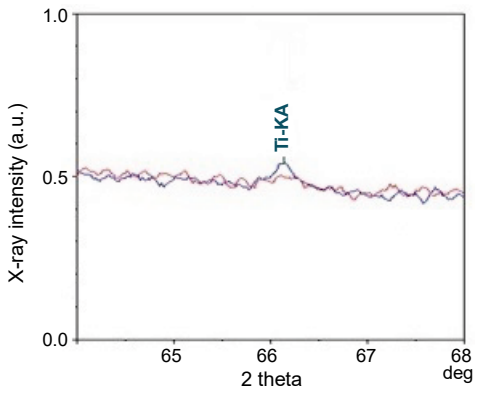


**Figure 1 Qualitative chart of Ti-Kα for polymer samples. Blue: 2.5 ppm, Red: 0.6 ppm**

## Analysis results

Figure 1 shows a qualitative chart of Ti-Kα for two samples containing a trace of Ti (2.5 ppm and 0.6 ppm). In this case, the software detected and identified a Ti-Kα peak. However, the software might not always be able to detect this peak for trace amounts. The counting time per step of a qualitative scanning measurement is very short, typically 0.2 seconds or shorter, not long enough to detect trace elements.

In the analysis for this application note, the fixed angle measurement was applied for Ti and V, where the counting time was 10 seconds each for peak and background. Longer counting time of the fixed angle measurement reduces statistical error, making the detection limit lower.

Table 1 shows SQX analysis results by fixed angle measurement and scanning measurement, together with quantitative analysis, where the counting time was 100 seconds each, by empirical calibration method for reference. Using the fixed angle measurement function, Ti and V concentrations less than 10 ppm can be detected, which are beyond the limits of detection by a scanning measurement, the standard measurement of the SQX program.

**Table 1 SQX analysis results together with empirical calibration results.**

| Sample | No.1 | No.2 | No.3 |
|---|---|---|---|
| **Titanium** | ppm | ppm | ppm |
| (1) Empirical calibration | 0.6 | 2.5 | n.d. |
| (2) SQX Fixed angle | n.d. | 3 | n.d. |
| (3) SQX Standard | n.d. | n.d. | n.d. |
| **Vanadium** | ppm | ppm | pm |
| (1) Empirical calibration | 1.7 | 3.9 | 9.0 |
| (2) SQX Fixed angle | n.d. | 4 | 10 |
| (3) SQX Standard | n.d. | n.d. | n.d. |

n.d.: not detected
(1) Quantitative analysis results by the empirical calibration method.
(2) SQX analysis results by the fixed angle measurement.
(3) SQX analysis results by the standard scanning measurement.

## Position of background measurement

In the fixed angle measurement, X-rays are counted at a peak and a background two-theta angle. The two-theta angle of the peak is determined based on the results of the previous scanning measurement. If a peak is detected, the two-theta angle of the detected peak is used; if not, the theoretical two-theta angle is used.

The background angle(s) is a certain number of degrees from the peak angle (Figure 2, a). However, if another peak exists at the background two-theta angle, the background intensity would be higher than expected (Figure 2, b). In the fixed angle measurement function, the software automatically determines a proper background angle by avoiding spectral overlap on the background position (Figure 2, b').

The SQX program also has a theoretical overlap correction function. Hence, when using SQX it is not necessary to manually separate peaks or change background angles; the software takes care of spectral overlap in SQX analysis.

## Conclusions

This application note shows that SQX, a semi-quantitative (standardless) analysis program, can give satisfactory analysis results for trace amounts of Ti and V in a polymer using the "fixed angle measurement" function.

SQX is a scanning-based program, where qualitative scanning charts are obtained. Therefore, it is possible to visually determine if elements of interest exist in a sample.

However, the counting time per step in a qualitative scanning measurement is very short, not enough long to detect trace elements.

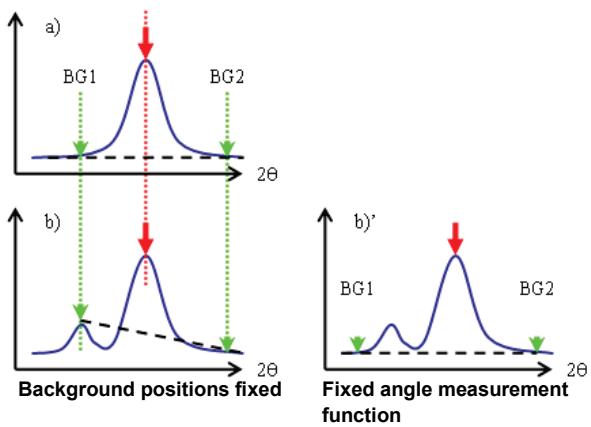


**Figure 2 Schematic diagram for the fixed angle measurement function.**

The counting time of the fixed angle measurement function of SQX, where the X-ray intensity is collected at a fixed two-theta angle for a user-specified time, is usually much longer than the counting time for a step in scanning, reducing the lower limit of detection.
Applying the fixed angle measurement function for SQX analysis can improve the precision for trace elements of interest in unknown samples.

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