

Benchtop total reflection XRF spectrometer

NANOHUNTER II



1. Introduction

X-ray fluorescence spectrometry (XRF) is well known as an analysis method with high precision by means of non-destructive and no contact analysis, and is therefore widely used for process and quality control at production sites.

In particular, total reflection X-ray fluorescence spectrometry (TXRF) developed in the 1970s is a special energy dispersive type XRF which excites elements only on the surface of sample.

TXRF has been one of the standard methods for wafer contamination analysis. However, TXRF has recently been gaining attention as a new technique for analysis of environmental samples.

Benchtop TXRF spectrometers are manufactured by

a few companies in the world, but no models other than the original NANOHUNTER has the highly advanced functions such as auto alignment of the optical system. The new TXRF spectrometer NANOHUNTER II, which is improved by the employment of newly developed components, is introduced here.

2. Features of the instrument

2.1. Realization of significantly higher sensitivity

The previous product employed a 50 W X-ray tube and composed the parallel optics with a multi-layer mirror and the Silicon Drift Detector (SDD). The new model is equipped with a high power 600 W X-ray source whose robustness has been proved in X-ray diffractometers. The focusing optics combines a

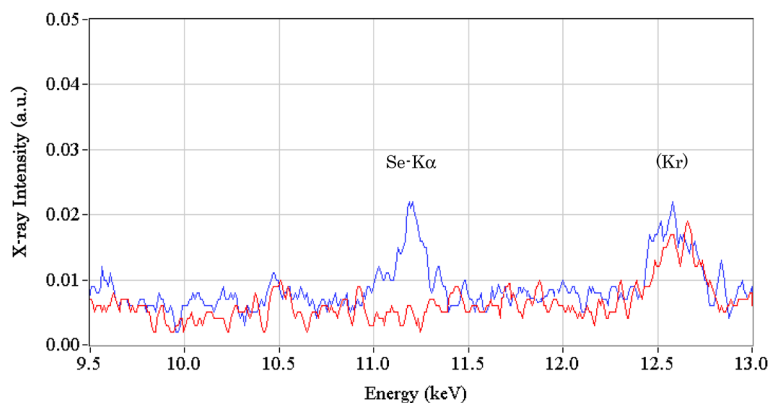


Fig. 1. Spectral chart of Se containing water solution. (Blue: Se10 ppb, Red: Glass substrate)

newly developed multi-layer mirror and incident slit. Moreover, employment of a new large diameter SDD system realizes 100 times higher sensitivity compared with the former model.

For example, Fig. 1 shows the spectral chart of a dropped and dried 10 μ L water solution sample containing ultra-trace amount of selenium (10 ppb) on a glass substrate. The Se-K α peak can be clearly seen for the sample which contains Se one order of magnitude less than the amount in effluent regulated by the Ministry of the Environment (Government of Japan).

The previous model was equipped with two X-ray tubes of Mo target and Cu target selectable for better excitation efficiency, but the new model is equipped with the Mo target tube only as the difference of excitation efficiency between Mo and Cu targets can be covered by the more than 10 times higher X-ray tube output, and the compatible peak spectra can be observed in the element range measured with Cu target in the previous model.

LLD (Lower Limit of Detection) for each element is shown in Fig. 2 below. 1 ppb (μ g/kg) of LLDs are achieved for various elements.

As a result of improved sensitivities, analysis with

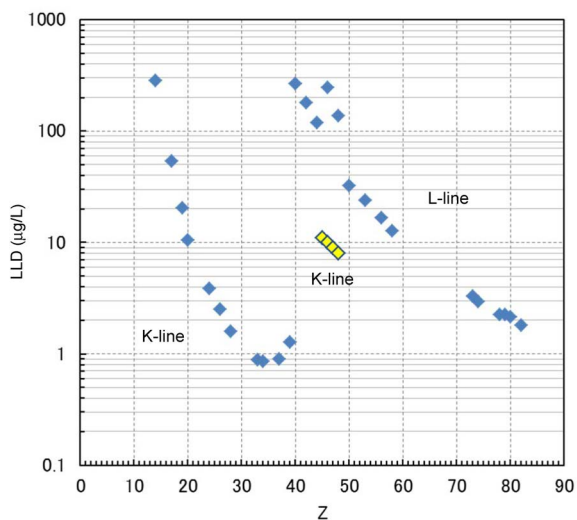


Fig. 2. LLD for each element.

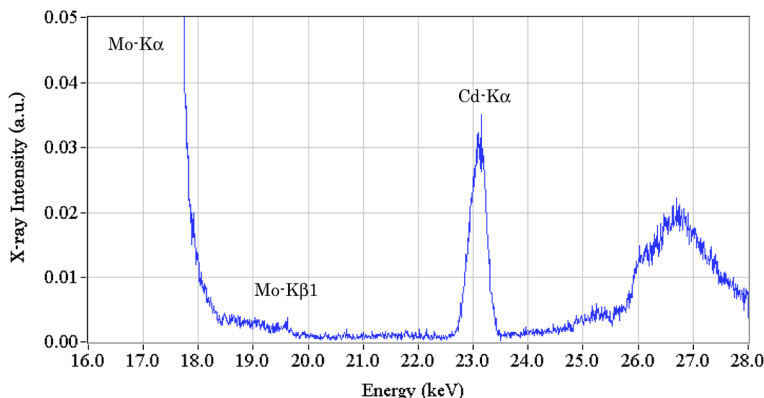


Fig. 3. K α -line spectrum of 1 ppm Cd.

1) lower LLD or 2) shorter measurement time can be performed.

2.2. Capability of high energy excitation (about 30 keV)

Standard excitation employs a multi-layer monochromator which monochromates the Mo-K α line (about 17.4 keV) to irradiate the sample. Conventionally, this multi-layer is designed to construct the alternate lamination of two element layers, namely, a heavy element to be a reflection layer and a light element works as a spacer.

A multi-layer monochromator is placed after X-ray tube to reflect only the Mo-K α line (17.4 keV) to irradiate the sample. In common multi-layer monochromators, heavy element layer (reflection layer) and light element layer (spacer layer) are coated alternatively. The new multilayer monochromator has been specially designed to reflect X-rays with two wavelengths of Mo-K α line and higher energy with about 30 keV. The higher energy X-rays can effectively excite K line fluorescent X-rays of heavy elements such as elements from Ru to Sn.

The measurement of K lines for these elements is very effective and good spectra with high peak to background ratio can be obtained since there are very few line overlaps. It also gives extremely low background in this energy range due to the principle of total reflection, whereas background is very high in conventional X-ray fluorescence spectrometry.

For example, Cd, which is the critical element for environmental analysis, used to be analyzed with L-line spectrum excited by the Mo characteristic X-rays in the past (Cu in case of former model). There were many occasions that the Cd-L line at about 3.1 keV cannot be easily detected due to overlap by the potassium peak (about 3.3 keV) common in environmental samples and the Ar peak at about 3.0 keV existing in the air. In contrast, the Cd-K line at about 23 keV has few overlapping spectra nearby and therefore allows easy detection of ultra-trace amounts.

Figure 3 shows the spectrum of 10 μ L water with 1 ppm Cd dropped and dried on a slide glass. The Cd

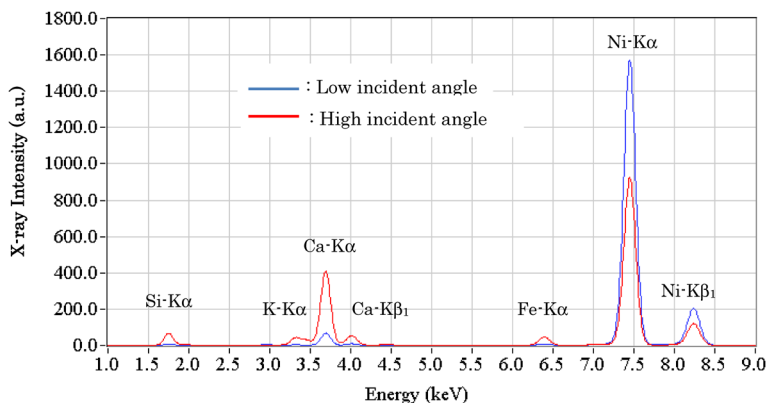


Fig. 4. Spectra from Ni thin film (25 nm) with glass substrate.

peak is clearly detected due to the low BG unique to TXRF instrument.

2.3. Variable incident angle

The incident angle auto adjustment was one of the essential optical adjustment functions to the original TXRF spectrometer. The function continues to be available on NANOHUNTER II.

The variable incident angle function also continues to be available which allows measurement with the optimal incident angle for any sample substrate which can have varying critical angles. Programmable driving of incident is a new feature which enables control of divergence angle.

Figure 4 shows the spectra of vapor-deposited Ni thin film (25 nm equivalent) on a glass substrate excited with different incident angles. When the incident angle is low, almost no peaks from the substrate is observed and the peak from the surface layer Ni is prominent. On the other hand, the peak intensity from the surface layer Ni decreases and the intensity of the substrate component increases for high incident angle. Only the elements located near the surface are excited efficiently in TXRF condition, and the information of deeper part can be obtained in high incident angle.

3. Application: Analysis of river water

The elemental analysis result of river water is shown below as an example. 10 μL sample added with Co as an internal standard element is dropped on an optical slide glass and dried. Measurement of the river water specimen resulted in detection of S, Cl, K, Ca, Fe, Br and Sr. Table 1 shows the quantification result of the detected elements. It can be seen that the

Table 1. Result of quantitative analysis of river water (ppm).

Z	TXRF	ICP-AES (A)	ICP-AES (B)
S	8.8	7.7	7.9
Cl	52.2	49.4	33 (IC)
K	13.4	8.43	6.7
Ca	28.9	20.7	22
Fe	0.51	0.0072 *	0.085 *
Br	0.14	0.054	<0.1 (IC)
Sr	0.081	0.071	

*Suspended solid is not included.

results are comparable to inductively-coupled plasma atomic emission spectrometry ICP-AES (partially by ion chromatography IC) measurement results at two laboratories (A, B).

4. Summary

The benchtop TXRF NANOHUNTER II is the superior instrument for material surface analysis of materials requiring high sensitivity. Although the most common applications are qualitative and quantitative analysis of trace element in liquids by means of dropping and drying, high sensitivity surface analysis of solid substances is also possible and therefore it is expected that it will be utilized by a wide range of users. Moreover, as it is also applicable as a grazing incidence X-ray fluorescence (GIXRF) instrument, this spectrometer can be a new evaluation apparatus which provides not only elemental analysis of sample surface but also elemental information for depth direction.