

## Detection of Trace Metals by Means of an Efficient Wavelength-dispersive X-ray Fluorescence Spectrometer

Trace metals sometimes play quite significant roles in spite of the extreme small amounts in which they exist, not only in industrial research but also in environmental and biomedical sciences. The synchrotron X-ray fluorescence technique [1] is a powerful probe for trace metals, and in particular, total-reflection X-ray fluorescence (TXRF) [2] using a mirror-polished substrate as a sample support, can detect trace metals with very high sensitivity. So far, an energy-dispersive spectrometer based on a Si(Li) detector has been employed, because of its high detection efficiency and tolerable energy resolution (130 ~ 170 eV for 5 ~ 10 keV X-rays) for separating X-ray fluorescence from the neighboring elements. However, there exist obvious limits in

detection power; the biggest problem is the scattering background, the low-energy-side tail of which severely restricts the detection of weak X-ray fluorescence signals. Therefore, one should note that upgrading the detection power is not always straightforward, even when brilliant sources are available.

A new idea comes with the use of wavelength-dispersive (WD) spectrometers to improve the signal to background ratio by eliminating scattering X-rays with enhanced energy resolution (Fig. 1) [3]. Since there is usually a trade-off between resolution and efficiency, one promising candidate is a spectrometer with downsized Johansson-type focusing optics with moderate energy resolution (~ 10 eV for 5 ~ 10 keV X-rays) [4-7]. Although another way to accomplish this might be to use conventional optics with flat crystals [8,9], the loss of detection efficiency can be a problem for trace analysis. Figure 2 schematically shows a wavelength-dispersive TXRF spectrometer, which is equipped with a Ge(220) analyzing crystal

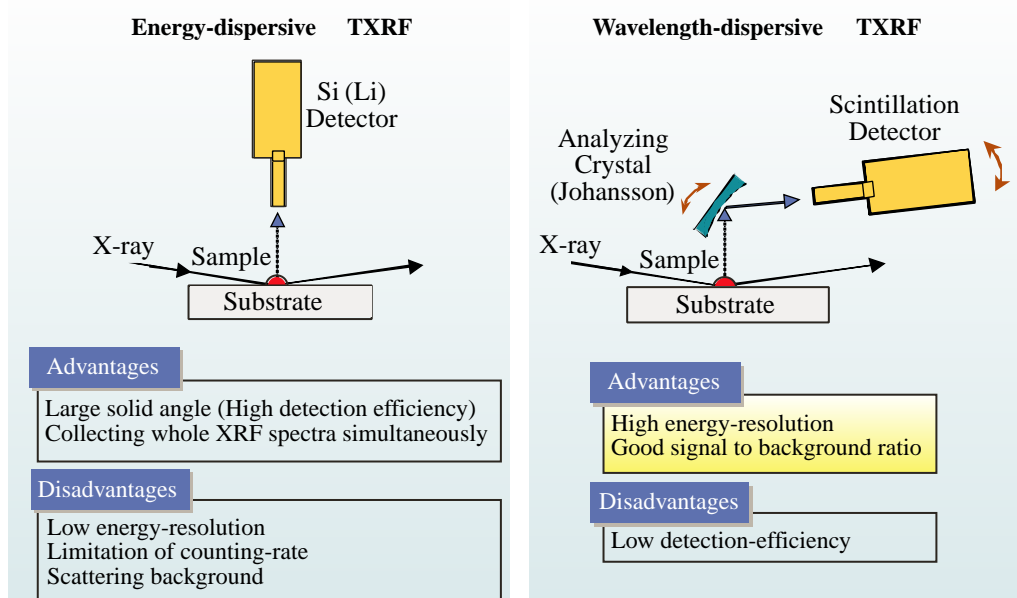


Fig. 1. Comparison between conventional energy-dispersive and the present wavelength-dispersive TXRF. The main idea of the present research is the employment of the Johansson-type spectrometer instead of a Si(Li) detector in TXRF experiments. The expected problem is low efficiency for ultra trace element analysis, but the present downsized spectrometer can solve it.

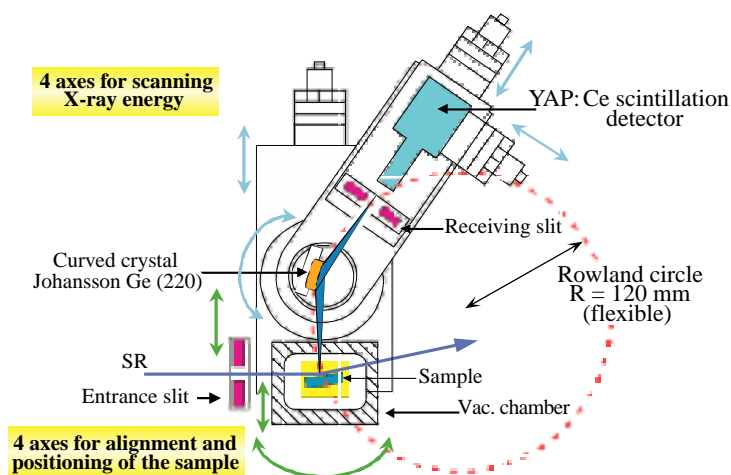


Fig. 2. Schematic view of the downsized Johansson TXRF spectrometer developed at Nat'l Inst. for Materials Science (NIMS), Tsukuba.

(Rowland radius 120 mm) and a YAP:Ce detector [10] with a 0.07 mm receiving slit. The most important feature is reasonably high detection efficiency with only a small loss of energy resolution [6].

Experiments have been performed at beamline **BL40XU** with quasi-monochromatic X-rays from a helical undulator source (ID gap 10.8 mm, fundamental peak 10 keV) and focusing optics

based on K-B mirrors (Fig. 3). The beam size used is  $30 \mu\text{m} \times 30 \mu\text{m}$ . Figure 4 shows typical TXRF spectra for a drop of liquid ( $0.1 \mu\text{l}$ ) containing 20 ppb Fe, Co and Ni. The scan requires 5 sec/point and the total measuring time is 10 - 15 min. The energy resolution is around 6 ~ 7 eV, around 20 times better than that obtained using a conventional energy-dispersive TXRF spectrometer. This

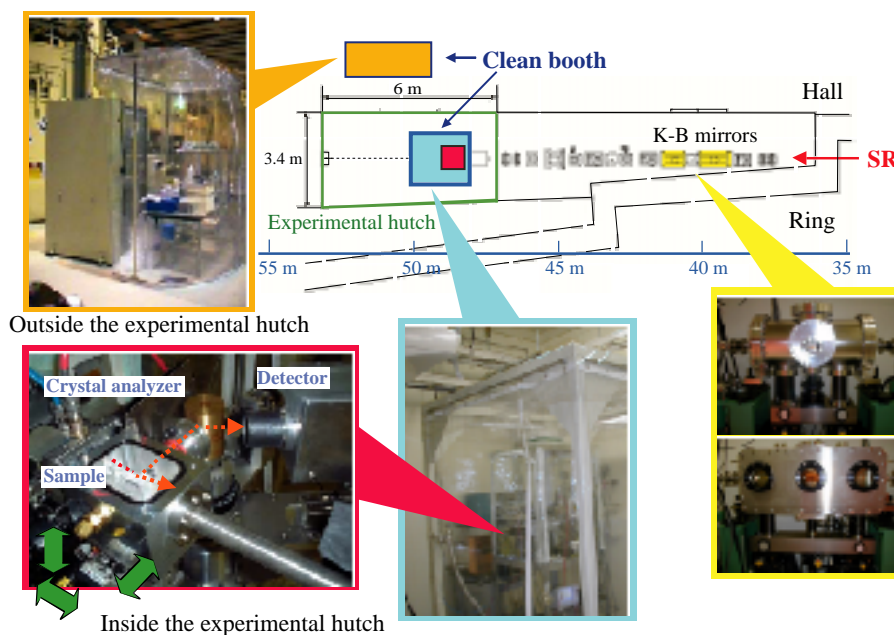


Fig. 3. Experiments setup at BL40XU. Combination of high-flux undulator beam and efficient XRF spectrometer.

contributed to reducing the influence of scattering background and X-ray fluorescence from the neighboring elements. Since the energy resolution is enhanced one can see even chemical effects by looking carefully in the area around  $K\beta$  spectra [7], which exhibit some satellite lines.

Figure 5 shows another result for Ni in a 0.1  $\mu\text{l}$  drop. The technique shows good linear relation in a wide dynamic range. The absolute detection limit obtained is 0.31 fg for Ni, and the concentration in a 0.1  $\mu\text{l}$  drop is 3.1 ppt, or further lower for a usual 1 ~ 50  $\mu\text{l}$  solution sample. The results are almost 1.5 ~ 2 decades better than the current best record performed with a Si(Li) detector [11]. The present technique is competitive with trace analysis, such as AAS and ICP-MS (Fig. 6). Besides extremely high sensitivity, capability of analyzing very small amount of samples is significant for practical analysis. Another

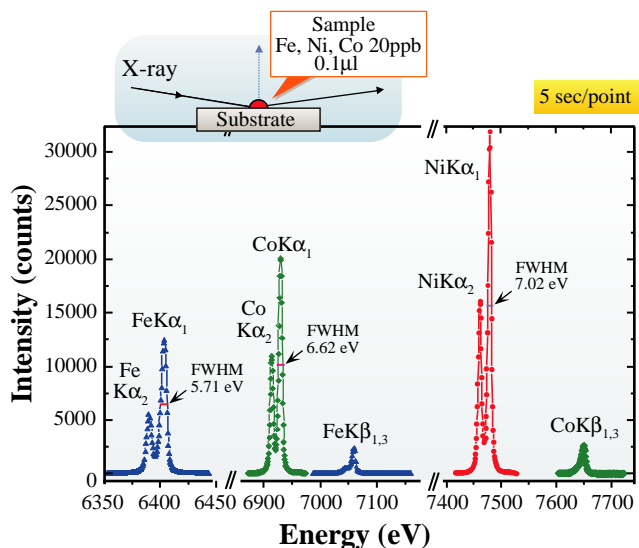


Fig. 4. Typical TXRF spectra for trace elements (Ni, Co and Fe, 20 ppb each) in a micro drop (0.1 micro liter). Details of the experiment are covered in the main text.

advantage is the non-destructive nature for the measurement. New opportunities for advanced analytical applications could be opened up.

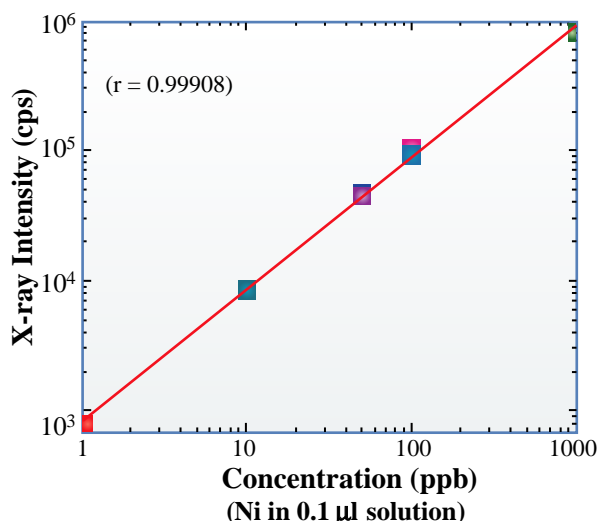
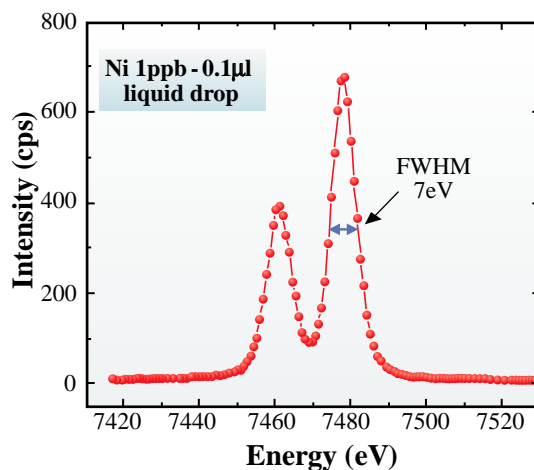


Fig. 5. Performance of the present wavelength-dispersive TXRF spectrometer; ppt level detection limit with less than  $\Delta E = 10$  eV.



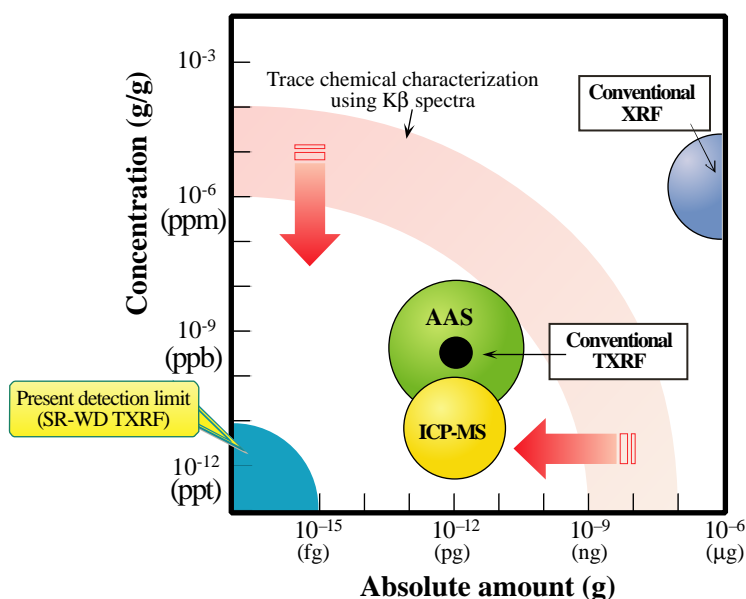


Fig. 6. Comparison of relative and absolute detection limits. Combination of the undulator source and the present TXRF spectrometer can provide the most powerful tool for trace element analysis. AAS: atomic absorption spectrometry; ICP-MS: inductively coupled plasma-mass spectrometry.

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