

# Liquid analysis by total reflection X-ray fluorescence spectrometer

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## 1. Introduction

Total Reflection X-ray Fluorescence (TXRF) is a method that can be used for high sensitive elemental analysis on solid sample surface, and has been widely used for detecting contamination on wafer to improve fabrication process yield in the semiconductor industry. On the other hand, there has been increasing need for liquid sample analysis such as contaminated water along with a movement to use TXRF analysis technique in the environmental field.

The TXRF analysis can reduce background intensity, because primary X-rays irradiated with very low glancing angle are totally reflected on the sample surface, and scattered X-rays do not enter the detector. Moreover, the spectra with high S/N ratio can be obtained since only the topmost sample surface is excited to generate fluorescent X-rays. Wide range of elements from Al to U can be analyzed qualitatively and quantitatively by the energy dispersive detector, and it is common to utilize built-in relative sensitivity coefficients for quantitative analysis without using standard samples. Actual example of quantitative analysis of liquid sample by TXRF is introduced in this report.

## 2. Outline of internal standard method

Generally, in liquid analysis by TXRF, the sample preparation is very simple. Drop small volume such as  $10\mu\text{L}$  on a substance and dry, and troublesome sample preparation is not required. In this preparation method, X-ray intensities are hardly influenced by coexisting elements, because analyzing depth of dried sample is negligibly small. Consequently quantitative analysis results can be easily obtained without correction for X-ray absorption. Quantitative analysis with TXRF is carried out occasionally using calibration curve made with standard samples, but rather often using internal standard method. In internal standard method, a certain amount of an element not contained in the sample is added as the internal standard element. And quantitative results of unknown elements are obtained utilizing the relative sensitivity coefficients mentioned above and known concentration of the internal standard element.

Sample preparation procedure of internal standard method is explained below.

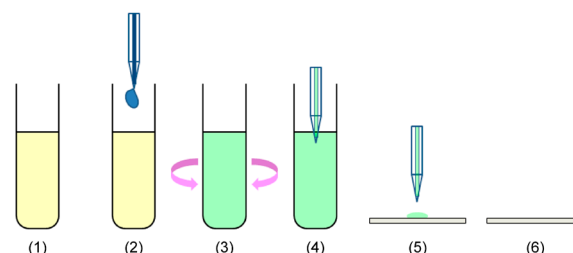


Fig. 1. Sample preparation procedure of internal standard method.

## Procedure

- (1) Take a certain volume of unknown sample
- (2) Add a specific volume of internal standard liquid of which concentration was adjusted.
- (3) Mix them well.
- (4) Take a certain volume of the mixture.
- (5) Drop it on a substrate.
- (6) Dry up.

As this is a very high sensitive analysis, it is necessary to pay attention not to get contaminated on chips of micropipette and other labware during this procedure.

The substrate can be selected according to analysis purpose, but it is often the case that surface-treated slide glass for making small dry mark is used. Sometimes a vacuum dryer is used to prevent the contamination when drying and shorten the drying time.

## 3. Example of quantitative analysis by internal standard method

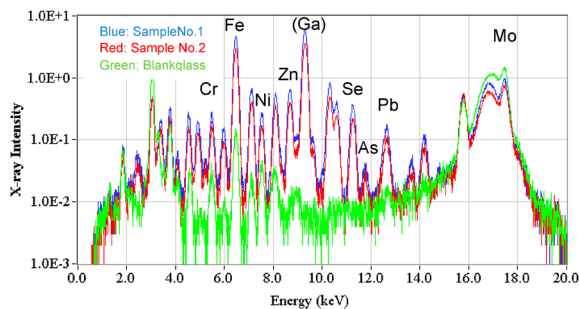
### 3.1. Application to environmental analysis

Need for the environmental analysis is increasing and various analysis methods have been developed and applied. Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) and Atomic Absorption Spectrometer (AAS) are widely applied for liquid analysis of river water or effluent. But it is well known that there are problems regarding disposal of waste liquid and running cost.

The example of environmental analysis with TXRF is introduced to show its comparable performance to those of ICP-OES or AAS.

Followings are the quantitative analysis results of a commercially available liquid standard solution by internal standard method.  $10\mu\text{L}$  of sample prepared according to the procedure mentioned above was dropped and dried on a substrate, and then analyzed as an unknown sample. 10ppm Ga was selected as an

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**Fig. 2.** Qualitative chart of liquid standard solutions containing Ga 10ppm.

**Table 1.** Quantitative analysis results of commercially available standard solution.

(ppm)	Std. value	+Ga 10ppm No. 1	+Ga 10ppm No. 2
Fe	15.3	16.5	17.4
Cr	1.0	1.25	1.29
Cu	1.0	1.08	1.11
Zn	1.0	1.07	1.07
Ni	0.5	0.60	0.63
Pb	0.5	0.28	0.30
Se	0.5	0.49	0.48
Mn	0.4	0.45	0.46
As	0.3	0.41	0.11
Ga	—	10.0	10.0

internal standard element. Figure 2 shows the qualitative analysis results of duplicated sample preparation and their good reproducibility.

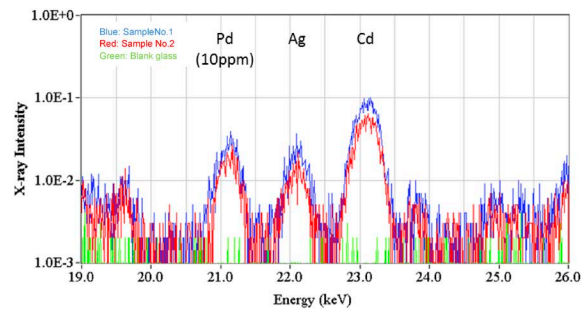
Table 1 shows the quantitative analysis results determined using the relative sensitivity coefficients based on the concentration of internal standard element (Ga). Good matching with the standard values is shown.

The quantitative analysis can be easily carried out by the internal standard method combined with TXRF, and TXRF spectrometer is expected for the environmental analysis applications of river water and effluent and impurities in tap water due to its low running cost.

### 3.2. Application to residual catalyst

In the R&D field of pharmaceutical products, effective evaluation method for small amount of precious sample is required, because only an extremely small amount of sample may be obtained experimentally. 1 mL of sample is sufficient for the sampling in TXRF and quantitative analysis can be made by employing the internal standard method.

It is known that the residuals of metal impurity elements such as Cd and Ag can substantially affect the human body or living organisms. L-line spectra of Cd and Ag are measured by general purpose TXRF spectrometer equipped with molybdenum target X-ray source. However it is reported that the elemental



**Fig. 3.** Qualitative spectra of Cd and Ag mixture solution samples.

**Table 2.** Quantification results of Cd and Ag mixture solution sample.

(ppm)	Std. value	No. 1	No. 2
Cd	30.0	27.7	26.8
Ag	5.0	4.6	4.5

identification is rather difficult, because the L-lines of these elements are overlapped with the spectra of coexisting light elements.

When a high energy excitation source of 30keV is employed instead of ordinary molybdenum K-line excitation, K-lines of Cd and Ag can be excited. In this K-line range, spectra without overlapping by coexisting light elements can be obtained, therefore, the spectra having high S/N ratio and low background can be obtained by TXRF condition.

A mixed water solution of Cd 30ppm and Ag 5ppm was prepared using standard solutions for AAS. And then Pd solution was added to the mixed solution such that Pd 10ppm is contained as an internal standard. Figure 3 shows the measurement results of two identical samples made by dropping and drying 10 $\mu$ L of the mixed solution.

No peaks can be seen in the high energy range spectrum, and clear peaks of Cd, Ag and Pb with good S/N ratio were obtained in spectra of the mixture sample. The quantification results determined with relative sensitivity coefficients based on the concentration of the internal standard element is shown in Table 2 below. Although some variations are observed, ppm level quantification can be made with very small amount of sample.

### 4. Conclusion

The TXRF analysis is not only known as a high sensitive elemental analysis method material on the surface of solid sample, but it is also applicable to the liquid sample analysis by appropriate sample preparation. The example of quantitative analysis by the internal standard method using the relative sensitivity coefficients is introduced in this report. The environmental analysis such as effluent is best suited for TXRF combined with internal standard method. This method is also expected to be applied for the trace element analysis in beverages such as drinking water and wine.