Reference-free X-ray fluorescence analysis

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Reference-free analysis is a new style of analysis that attempts to achieve the same effect on quantitative analysis without the use of experimental calibration curves using a group of standards. Among the numerous techniques of elemental analysis, X-ray fluorescence analysis is the top runner in reference-free analysis. It is important that all the physical processes and characteristics of the instrumentation are well understood, that most of them can be expressed in theoretical formulas, and that the results are sufficiently predictable to correspond to the chemical composition of the sample. However, in reality, it is often handled in a black-box manner by non-specialists, and there is a risk of inadequate analysis values being taken alone. An international conference on physical constants (fundamental parameters) of X-rays for reference-free analysis held in the autumn of this year led to the formation of an alliance consisting of 11 private companies, AIST and NIMS, which is working on the development of reliable reference-free X-ray fluorescence analysis.

1.Introduction

Many elemental analysis methods, including X-ray fluorescence analysis, are customarily performed using the relationship between the signal intensity (X-ray fluorescence intensity) and the concentration or absolute amount, called a calibration curve. Since it is necessary to take the so-called matrix effect into account, a single calibration curve cannot be applied to all samples by chance. In order to obtain a calibration curve, it is necessary to have a group of standard samples that are very similar to the main components of the unknown sample, and in which the concentrations and absolute amounts of the elements of interest are systematically varied. Standard samples need to be prepared for each of the different analytes. This has been considered to be an essential requirement for quantitative analysis.

The prerequisite for reference-free analysis is that all the physical processes and equipment involved in the measurement are well understood, most of them can be presented in theoretical formulas, and all effects, including matrix effects, can be adequately predicted. The most advanced reference-free analysis at present is the X-ray fluorescence method. The reason for this is that the principle is relatively simple and the theory [1)-4)] were developed more than 60 years ago, and then computers were developed and are now readily available to everyone. Although most chemical analysis methods are still at the stage of requiring the adoption of calibration methods, we can safely assume that they are moving in the direction of quantitative analysis with reference-free analysis as an option, even 50 or 100 years into the future.

In this article, we report our efforts on the reliability of reference-free X-ray fluorescence analysis.

2. Certified reference material as a reliability tool

X-ray fluorescence analysis is a method of analyzing the chemical composition of a sample by measuring the element-specific X-rays emitted when the sample is irradiated with primary X-rays. A calibration curve plotting the relationship between elemental concentration and X-ray fluorescence intensity is usually used for the quantitative analysis. Since the X-ray fluorescence intensity depends not only on the concentration of the elements but also on the chemical composition of the matrix, it is necessary to prepare standard samples with similar matrices and known concentrations of the elements in advance and to measure the X-ray fluorescence spectra in order to generate a calibration curve. On the other hand, it is not always easy to prepare such a set of reference materials that are highly similar to the reference materials in some fields of application. In such cases, reference-free X-ray fluorescence analysis is very useful. Reference-free X-ray fluorescence analysis is a method that corrects matrix effects mainly by using the Sherman's formula [1)] or Shiraiwa-Fujino's formula [2)], which is also known as the Sherman's formula, in order to obtain practically the same effect as the calibration method. The simplicity and ease of operation of quantitative analysis

is advantageous for its application. Recently, many hand-held mobile-type X-ray fluorescence analyzers, which are battery-powered and portable, have also been introduced to reference-free quantitative analysis, and the range of applications has expanded to an unprecedented extent. As a result, it is not uncommon for non-specialists to perform analyses and handle the results without being familiar with the inner workings of the instruments and software. It is a risk factor for our society that analytical values produced by computers are walking by themselves, and this creates an unstable situation in which no one can have confidence in their support. This is a particular concern in the field where there is no expert in analysis.

One of the ways to confirm the reliability of reference-free X-ray fluorescence analysis performed on all X-ray analytical instruments scattered throughout Japan is the development and dissemination of certified reference materials that are common and usable throughout the country. A certified reference material (CRM) is "a reference material that has been calibrated in a metrologically valid procedure with respect to the concentration and absolute amount of each element in order to determine the measurement values in chemical measurements, such as the calibration of analytical instruments and the evaluation of analytical methods". The National Institute of Standards and Technology (NIST) in the U.S., which has a document called a certificate of certification attached to each CRM, which describes the concentration and absolute amount of each element, as well as its uncertainty and metrological traceability, is well known and is circulating throughout the world, and in Japan, AIST is systematically developing it. In addition, the Japan Society for Analytical Chemistry (JSAC) has developed useful reference materials for X-ray fluorescence analysis by Toshihiro Nakamura and others at Meiji University. In the conventional calibration method, a calibration curve is generated using a reference standard whose matrix composition is similar to that of the sample being analyzed and whose concentration and absolute amount of the element of interest are systematically varied. Although reference-free X-ray fluorescence analysis does not require a reference sample in this sense, the reliability can be ensured by actually measuring the certified reference material and checking whether a predetermined value is obtained or not, thereby providing confirmation of the validity of the equipment and measurement conditions employed.

More specifically, in reference-free fluorescent X-ray analysis, certified reference materials have at least the following three uses.

(1) Validity verification of analytical values
(2) Calibration of sensitivity coefficient
(3) Confirmation of stability of routine analysis

(1) Validity verification of analytical values means to check and confirm the validity of analysis of a sample having a composition or layer structure that is almost the same as or very similar to the certified reference material, before and after the measurement of the sample. Substances should also be measured under the same conditions.

(2) Calibration of sensitivity coefficient is to register the data of certified reference material in the software of the instrument, and correct the sensitivity coefficient so that the difference between the analytical value and the certified value obtained by the software of the instrument is minimized. It is to be. However, before performing this calibration, if the analytical value obtained by measuring the certified reference material and the certified value are too different, it is necessary to first check whether the analytical conditions and measurement conditions are appropriate. desirable.

(3) Confirmation of the stability of the routine analysis is to confirm and control the correctness of the daily routine analysis by periodically measuring the certified reference material and confirming the repeatability of the obtained spectra and analytical values. In doing so, reference should be made to the expanded uncertainties described in the certificate. Uncertainty is inherent in every measurement, but it is possible to control the variability of each factor (standard deviation of repeated measurements). The square root of the sum of the squares of the uncertainties of all factors is the standard combined uncertainty, and the expanded uncertainty is the one multiplied by a coefficient, taking into account the confidence intervals and so on. It is common to use a coefficient of 2 and to present it as half the value of an interval with a level of confidence of about 95%. The certificate accompanying the certified reference material also contains the above explanation. The treatment of uncertainties etc. is detailed in a document published by European Union of Analytical Chemistry (Eurachem) [5] (Japanese translation [6] have also been published).

3. Experience of round robin test [7,8)]

In Europe since 2008, an EU project led by the the Physikalisch-Technische Bundesanstalt (PTB) in Germany and the National Metrology Laboratory in France (Laboratoire National de meteologie et d'essais, LNE) has been carried out by the FP international initiative (International initiative on X-ray fundamental parameters) is in progress. The main purpose of this project is to expand the physical constants of X-rays used in reference-free analysis by experiments such as synchrotron radiation or by theoretical calculations, and to build a better database in terms of accuracy than ever before. We are in constant contact with the Japanese members in the field of X-ray analysis and have been working together with them. While in Europe, the main effort is to enrich and complete the table of x-ray physics constants, the activities in Japan have some characteristics that are different from those in Europe. Our main goal is to innovate through the improvement of the reliability of reference-free X-ray analysis, and we focus on the solution of various analytical problems and try to develop certified reference materials and similar knowledge and techniques, while paying high attention to the problem of the X-ray physical constants.

Major Japanese companies, user companies and national research institutes in Japan have been collaborating since around 2012 and have been continuously discussing the issue of how to improve the reliability of reference-free X-ray fluorescence analysis.

In 2016, 11 private companies (Bruker Japan K.K., Horiba Ltd., Rigaku Corp., Techno X Co., Ltd., Shimadzu Corp., Toshiba Corp., Hitachi High-Tech Science Corp., JEOL Ltd., Toshiba Nano Analysis Corp., Canon Inc., Spectris Co., Ltd., PANalytical Division) and two national research institutes (AIST, NIMS) conducted round-robin tests using common samples of metal multi-layer films, which are supposed to be used in applications such as plating to improve the reliability of reference-free X-ray fluorescence analysis, as a part of all-Japan activities. Two samples (Sample 1, Sample 2) were distributed and one company measured them every week, and after the measurement was completed, they were returned to the management organization (NIMS) and measured by another company the following week, this work was done for 11 consecutive weeks. Although it is a simple type of round-robin test, it is also called a pedal type because the company returns the test to the management institution once to ascertain any changes during the circulation.

The common specimens used in the round-robin tests were composed of gold/nickel/copper layers on chrome-coated quartz glass substrates. The samples were later certified by the National Metrology Institute of Japan (NMIJ) of AIST (cross-sectional observation of the samples by scanning electron microscopy and chemical analysis (inductively coupled plasma optical emission spectrometry (ICP-OES), ICP mass spectrometry (ICP-MS), and isotope dilution ICP-MS), and in May 2017, the certified reference material NMIJ CRM It was distributed as 5208-a. Two values are certified for each layer: shape film thickness and areal density (often referred to as mass film thickness in X-ray fluorescence analysis). This round-robin test was conducted long before such a valuation was made. Participants in the round-robin test may use any X-ray tube, output, filter, detector, etc. in making their measurements, and the reported results are only the mass film thickness of each layer for the two samples.

Figure 1 shows the round-robin test results. Although 11 companies participated, some companies reported the results of analysis using multiple instruments and multiple spectrometers (wavelength dispersion type and energy monodispersion type, etc.), resulting in a total of 15 data sets. The Grubbs test3) examined both the cases where two data were excluded and the case where they were left. Table 1 corresponds to the result of collecting 13 data excluding 2 data. As a result of the examination, the following points were immediately revealed.

Firstly, although the measurements were made independently under different conditions with different equipment and different analytical fields of view, the scatter in the reported values was within the range of 5-8% for all samples and strata, showing that the results were very good. Since reference-free X-ray fluorescence analysis is not based on calibration curves made from a set of standard samples, many experts have been concerned about the variability of the analysis values, but in reality, such good accuracy (reproducibility and stability) can be achieved.

Secondly, it is of great interest to know how close the obtained value is to the true value or to the analytical value obtained by other methods. In comparison with the chemical analysis of Sample2, it seems that X-ray fluorescence analysis tends to give a higher value than destructive analysis, but the difference is within a few percent at most. Considering the fact that the uncertainties in the three layers

	XRF		Chemical analysis
	Sample 1	Sample 2	
1st layer (Au)	0.187 ± 0.008 4.3%	0.184 ± 0.008 4.3%	0.184 (0.005)
2nd layer (Ni)	0.921 ± 0.059 6.4%	0.900 ± 0.059 6.6%	0.869 (0.017)
3rd layer (Cu)	0.909 ± 0.048 5.3%	0.907 ± 0.053 5.8%	0.880 (0.014)

Table 1. Round-robin test results [7)]

Sample 2 later became a certified reference material. Indicates the chemical analysis value used to obtain the certified value and the expanded uncertainty (in parentheses)

of the chemical analysis are 2.7%, 2.0% and 1.6% from the top to the bottom, respectively, the degree of agreement is rather good.

Thirdly, from the experience of a similar test that was performed before this round robin test, there was concern that the sample might change over time before the test. Due to the difference in thermal expansion coefficient between the metal thin film and the quartz glass substrate, the relatively thick film is easily peeled off during the hot summer months. No such changes were observed in the values reported in this round robin test. A slight stain was found on the surface of the sample when inspected and observed weekly, but no sign of peeling of the sample was observed. It was confirmed that the standard substance prepared this time is resistant to aging.

Fourth, although the companies participating in the round robin test were not known in advance, Sample l and Sample 2 have different coating conditions, and although there are slight differences, such differences are also observed in the round robin test. It was confirmed from the results. Sample 1 has a distribution (slope) depending on the location, but some participating companies report the results of non-uniformity evaluation by X-ray fluorescence mapping, and almost all understanding is X. It was made non-destructive only with lines. As described above, the round-robin test provides non-destructive, reference-free X-ray fluorescence data with extremely high reliability, and the importance of owning and usefulness using such samples on a daily basis.

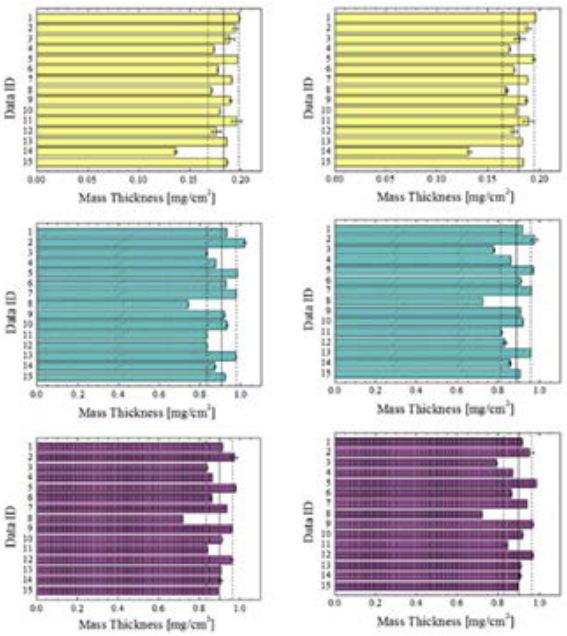

Figure 1 Round robin test results [7)]

Fifteen datasets were reported by 11 companies participating in the round robin test. The left is the result of Sample1 and the right is the result of Sample2. From top to bottom is the mass thickness of gold, nickel, copper

4. Summary

In the field of X-ray fluorescence analysis, a new analysis style called reference-free analysis was realized ahead of other analysis methods, and it is still developing. Reference-free analysis can be used even when it is not possible to prepare in advance a standard sample group whose matrix composition is very close to that of the analytical sample, because the same effect can be obtained without using an experimental calibration curve in quantitative analysis. Because of this great advantage, the field of application will continue to expand in the future.

The author recently published a book on reference-free X-ray fluorescence analysis [9)] with participants in the round robin test. It is the world's first book on reference-free X-ray fluorescence analysis. We hope that those who are interested can pick it up.

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