

Foreign material analysis using energy dispersive X-ray fluorescence spectrometers

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1. Introduction

As a handy and quick elemental analysis technique, X-ray fluorescence spectrometry is widely used in many industrial fields. It should be noted that energy dispersive X-ray fluorescence (EDX) spectrometers provide opportunities for miniaturization, because their system configuration does not require a dispersive element or goniometer. In addition, because of their ability to analyze multiple elements simultaneously, these spectrometers demonstrate their superiority especially when a sample of unknown identity needs to be analyzed quickly. One of the best examples of this is analysis of foreign materials mixed into products.

In recent years, safety awareness is increasing among consumers. If by any chance a foreign material is spotted in a product after shipment, the product manufacturer will be required to analyze the foreign material and to identify the route of contamination quickly and accurately. There are several types of techniques used for analyzing such foreign materials, but EDX spectrometers are excellent, especially in handiness and promptness, and are considered best suited for this type of analysis.

In this report, methodologies associated with analyzing foreign materials, using NEX DE energy dispersive X-ray fluorescence spectrometer, will be described. In addition, several examples of analyzing specific foreign material samples will be described.

2. Sample preparation

In many foreign material analyses, only a small amount of the object subject to measurement is available, or such object is embedded in a large-size

product. There are also many cases in which sample cups and pressure forming used for conventional X-ray fluorescence spectrometry cannot be applied to foreign material analysis. In this chapter, several examples of sample preparation often used for foreign material analysis will be introduced.

2.1. Using small-diameter sample cups

When the object subject to measurement has small quantity of powder or a small piece in it, it may be difficult to measure in a typical sample cup with an inner diameter of 24.6 mm [Cat.No.CH1330]. This includes a sample moving toward the edge of the cup and out of the analysis area. In such a case, the use of a small-diameter sample cup as shown in Fig. 1 would allow one to properly retain a sample with a small diameter or small quantity. Figure 2 shows a schematic cross-section of a small-diameter sample cup. These small-diameter sample cups come in four sizes with different inner diameters: 6 mm, 10 mm, 15 mm, and 20 mm [Cat.No.CH3106, CH3110, CH3115, or CH3120]. The best-suited one may be selected depending on the amount of sample subject to measurement.

2.2. Sandwich method using two films

If a special small-diameter sample cup is not available, the sample may be retained by sandwiching it between two films held by the above-mentioned conventional sample cup [Cat.No.CH1330], as shown in Fig. 3. Figure 4 shows a schematic cross-section of this setup. Due to the load exerted onto the film surface, this technique is not suited for thick samples, such as gravel, but it can satisfactorily retain a thin sample such as a



Fig. 1. Small-diameter sample cups.

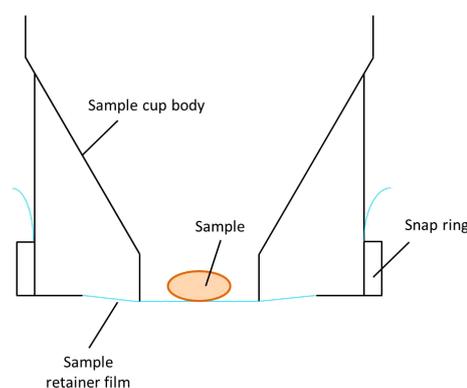


Fig. 2. A schematic cross-section of a small-diameter sample cup.

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Fig. 3. Sandwich method.

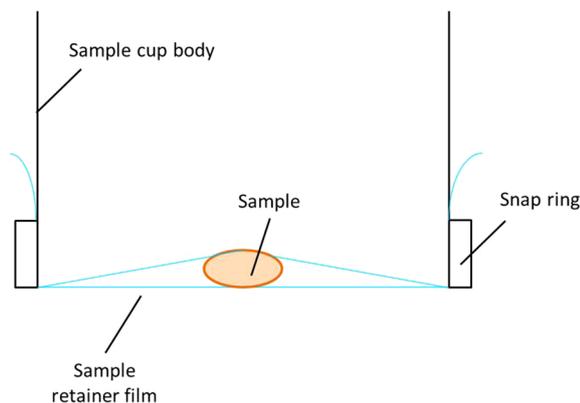


Fig. 4. A schematic cross-section of the sandwich method.

metal piece or powder in a small quantity. If a vacuum environment analysis is required for better performance of low atomic number elements, it is recommended to make small holes in the film in four corners using a pin to prevent the cup from bursting.

In addition, you can use a special sample cup designed to reduce the influence of scattered radiation [Cat.No.RS1340].

2.3. Direct sample placement

When the object subject to measurement is embedded in a large-size product that does not fit into a sample cup, the whole product may be placed onto the floor of the sample chamber for measurement, with the automatic sample changer detached from the device. Figure 5 shows the sample chamber of Rigaku NEX DE energy dispersive X-ray fluorescence spectrometer. Measurements can be done so long as the sample fits into this space, with the sample sitting directly on the chamber floor and without the need for special sample preparation. Furthermore, it is possible to measure the composition of foreign material without physically removing it from the product. This can be done by comparing the qualitative analysis spectrum of the area of the foreign material embedded in the product with that of the surrounding area. The measurement point can be set easily using a sample observation camera, which will be described in the next chapter.

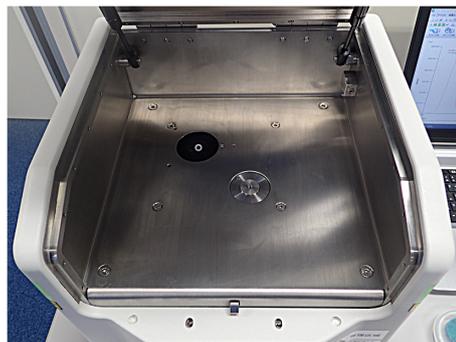


Fig. 5. Sample chamber of NEX DE.

3. Using a sample observation camera

Assuming possible application to foreign material analysis, many of the recent EDX spectrometers are configured with a sample observation mechanism, which allows a measurement point to be set by observing the sample surface with a camera. As an example, the point analysis function of the NEX DE will be explained below. Figure 6 shows the point analysis screen of the NEX DE Windows based analytical software.

On NEX DE, a measurement point diameter may be selected as appropriate for each application: 10mm, 3mm, or 1mm. By using the point analysis function, each measurement point is highlighted by a red sphere on the sample image taken by a camera, which makes it possible to analyze even small foreign material.

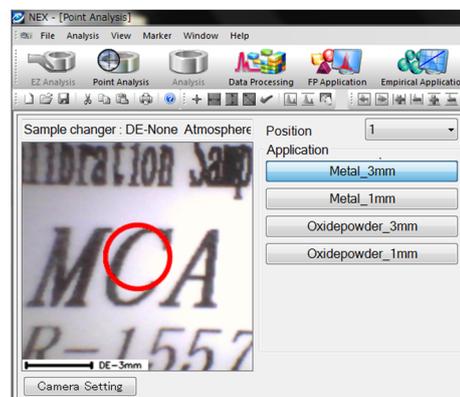


Fig. 6. Point analysis function.

4. Using FP-based semi-quantitative analysis

It is common that EDX spectrometers employ semi-quantitative analysis (SQX analysis), which calculates quantitative results using a FP (fundamental parameters) method. Of course, SQX technique can be applied to foreign material analysis, but there are several notes of caution. In this chapter, precautions for SQX analysis, when applied to foreign material analysis, will be described.

4.1. Sample model selection

Because SQX analysis is based on the FP method, calculation requires the selection of a sample model

depending on the type of the sample subject to measurement. It is easy to select sample models for typical analyses on an EDX spectrometer because the identity of samples is known to some extent. In reality, however, there are many cases where foreign material analyses are conducted on samples of completely unknown identity, which makes the selection of sample models somewhat difficult. The following is a simple guideline for the selection of analytical models used for SQX analysis of foreign material samples. If you are using the aforementioned Rigaku NEX DE, the pre-installed analysis templates may be used for the selection of analytical models. Possible sample forms and the corresponding analysis template best suited for each form are described below.

(1) The foreign material sample is considered to be metal because metallic luster is observed on the surface

When the foreign material seems to be a metal, the sample is judged not to contain large amounts of immeasurable elements. In such a case, it is desirable to use a sample model that assumes all detected elements to be single elements. If you are using NEX DE templates, it is recommended to use a template for "metal."

(2) The samples are powdery with no metallic luster and are considered to be an oxide

When the main component of the foreign material is an oxide, the large amount of oxygen (O) contained in the material is not directly detectable. In this case, oxygen should be added to the balance component when selecting a sample model, or a sample model designed to detect oxides should be selected. If you are using NEX DE templates, it is recommended to use a template for "powder" or "oxide powder." But when the sample diameter is smaller than the measurement point diameter, the use of a template for "oxide powder," which treats the components as oxides, will bring better results in many cases than the use of a balance component. Details will be described in the next section.

(3) The sample is expected to contain large amounts of organic substances

Similarly to the case of oxides described above, when samples contain large amounts of organic substances consisting of carbon (C), hydrogen (H), and other elements which have atomic number lower than Sodium (Na), it is not possible to directly detect X-ray fluorescence peaks of these elements. For this reason, it is desirable to use a sample model designed to set an organic component as the balance component. If you are using NEX DE templates, it is recommended to use a template for "powder" or "polymer (pellet)" with modifications to the balance component depending on the type of the sample. When the sample contains large amounts of organic substances, X-ray intensity may be affected depending on the thickness of the sample. In this case, sample thickness correction may provide effective compensation.

4.2. When the sample has a diameter smaller than the measurement point diameter selected

The size of foreign material samples varies depending on the sample type, and in some cases it is smaller than the minimum measurement point diameter of 1 mm. Generally, it is not desirable to measure the size of a sample smaller than the measurement point diameter in X-ray fluorescence spectroscopy because it will affect X-ray intensity. However, SQX analysis is normalized so that the analysis results of all elements will total 100%, which means errors from sample size will be automatically corrected, and this situation seldom causes a significant problem. This advantage makes it possible to analyze small-size samples with a diameter less than 1 mm using the same procedure as much larger size samples, and it is also possible to obtain SQX analysis results with the same level of accuracy.

However, the above description does not apply to sample models which contain a balance component. When a balance component is set in a sample model, analysis results will be calculated so that they will total 100% (including the balance component), instead of being normalized as described above. This means that when the sample is smaller than the measurement point diameter, its analysis results may be underestimated. For this reason, when conducting SQX analysis of a sample that is considered to be an oxide, it is recommended to use a template for "oxide powder," which does not contain a balance component, instead of using a template for "powder" that specifies oxygen as the balance component.

5. Examples of analyzing foreign materials mixed into food

In this chapter, examples of applying the above-mentioned analytical methods to real samples will be explored.

5.1. Analyzing a stone chip mixed into rice grains

As agricultural products are produced in environments close to nature, environmental-origin foreign materials such as pieces of stone and insects are occasionally seen mixed into these products. With safety awareness increasing amongst consumers in recent years, a number of measures are being taken to abate this type of problem, including mechanical separation and through visual inspection. Still, it is very difficult to eliminate such foreign material contamination. This is why the identity of foreign materials and the route of contamination must be investigated as part of post-contamination procedures.

As shown in Fig. 7, a stone-chip-like foreign material was spotted in rice grains distributed in the market. The foreign material was taken out using tweezers and analyzed in a small-diameter sample cup, which was described in Section 2.1. (Fig. 8). Prior to our SQX analysis, the appearance of the foreign material was inspected visually. The contaminant did not



Fig. 7. A stone-chip-like foreign material mixed into rice grains.



Fig. 8. The stone-chip-like foreign material placed in a small-diameter sample cup.

have metallic luster and looked like stone. From its appearance, it was judged that the foreign material was not a metal but rather an oxide. Then, SQX analysis was conducted using a sample template for “oxide powder,” and by setting the measurement point diameter at 3 mm and the measurement time at 1 min per sample. Figure 9 shows the spectrum obtained from this analysis.

The detection of a high peak of Si-K α line indicated the presence of a large amount of Si in the foreign material measured. Also detected were trace amounts of elements often seen in rock and soil such as Rb, Sr, Y and Zr.

Table 1 shows the result of SQX analysis of the stone-chip-like foreign material, which was calculated from the spectrum shown in Fig. 9.

Table 1. SQX analysis result of the stone-chip-like foreign material (main components only).

Component	Content (mass%)
SiO ₂	74.9
CaO	9.25
Al ₂ O ₃	8.80
Fe ₂ O ₃	1.35

From the elements detected in Fig. 9, the quantitative analytical results in Table 1, and the appearance of the contaminant, it was concluded that the stone-chip-like foreign material mixed into the rice grains was a stone chip whose main component is silicon dioxide. Although the route of contamination is still unknown, it is possible that a stone chip mixed into rice grains during harvesting remained in a plastic bag without being rejected in the packing process.

5.2. Analyzing white foreign material attached to a cracker

In actual foreign material contamination, there are cases where foreign material is firmly adhered to a product, making it difficult to separate them. In such a case, the use of a point analysis function will enable identification of the elements contained in the foreign material, by comparing the spectrum of the foreign material area with that of the surrounding area.

As shown in Fig. 10, a simulated foreign material sample was prepared by intentionally attaching white paint onto a commercially available cracker. This simulated sample was placed (as is) in the sample chamber of an X-ray fluorescence spectrometer to compare the X-ray fluorescence spectrum of the white paint area with that of another area on the surface using the point analysis function. Figure 11 shows characteristic peaks of the spectra obtained.

As a result, strong Ti- and Zn-derived fluorescent X-ray peaks were detected only from the area of the white paint deposit, which indicates that the area contains large amounts of Ti and Zn. It is generally known that titanium dioxide and zinc oxide are widely used to produce white pigments. Based on these X-ray fluorescence spectra, it was inferred that some kind of paint was attached to the cracker.

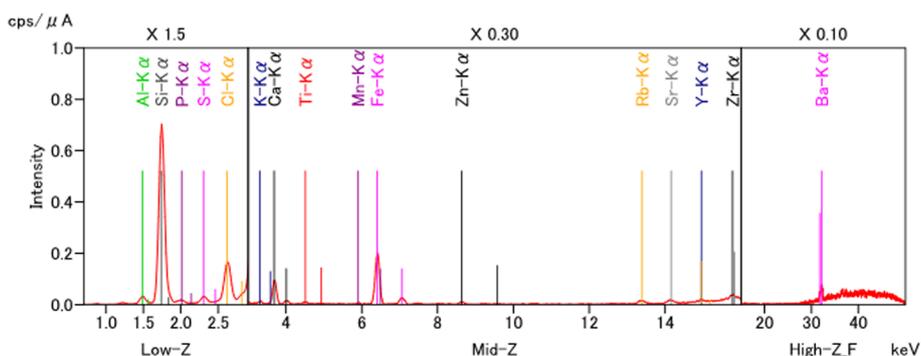


Fig. 9. An X-ray fluorescence spectrum of the stone-chip-like foreign material.



Fig. 10. White foreign material on a cracker.

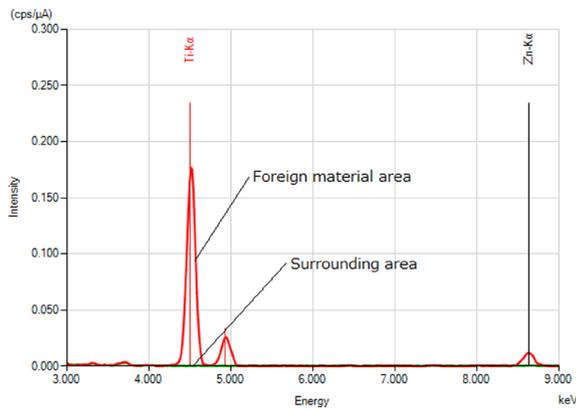


Fig. 11. X-ray fluorescence spectrums of the foreign material attached to the cracker and the surrounding area.

5.3. Analyzing a piece of metal mixed into process cheese

Foreign materials mixed into food sometimes cause serious customer complaints. One of such examples is that a consumer gets injured in the mouth because of a piece of metal mixed into food.

As a sample representing this type of problem, a simulated sample was prepared by embedding a small piece of metal into a commercially available block of processed cheese. Figure 12 shows the photo of the simulated sample. Similarly to the above-mentioned cracker analysis, this foreign material sample was measured (as is) to compare the X-ray fluorescence



Fig. 12. A piece of metal in a block of cheese.

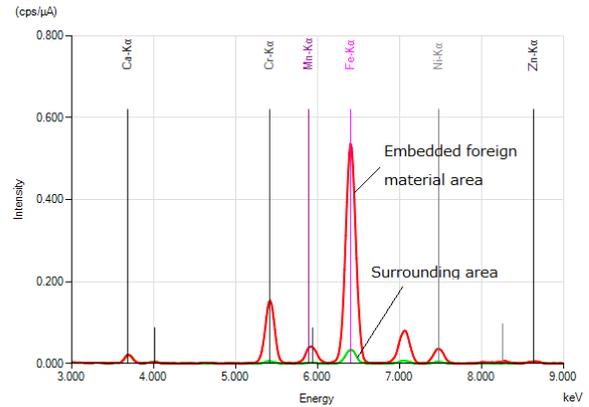


Fig. 13. X-ray fluorescence spectra of a foreign material embedded in the cheese and the surrounding area.



Fig. 14. The piece of metal taken out from the cheese.



Fig. 15. The piece of metal sitting in a sample cup.

spectrum of the imbedded metal with that of the surrounding area. Figure 13 shows characteristic peaks of the spectra obtained.

There were peaks of metal elements such as Cr, Mn, Fe and Ni that were not detected in the surrounding area. Based on this observation, it was inferred that the foreign material is a metal whose main components are these elements.

Then, semi-quantitative analysis was conducted for further investigation. As shown in Figs. 14 and 15, the piece of metal was taken out from the block of cheese using tweezers, and it was retained in a standard sample cup, sandwiched between two films. Because the surface clearly had metallic luster, the foreign material was

Table 2. SQX analysis results of the piece of metal (main components only).

Component	Content (mass%)
Fe	71.2
Cr	16.9
Ni	6.92
Mn	2.52

Based on these results, the piece of metal was found to be a stainless-steel-based material whose main component is Fe. Meanwhile, NEX DE is equipped with a material identification function that is designed to retrieve a number of materials registered as standards based on the results of quantitative analysis. By using this type of software feature, it is possible to determine the material of the contaminant as shown in Fig. 16.

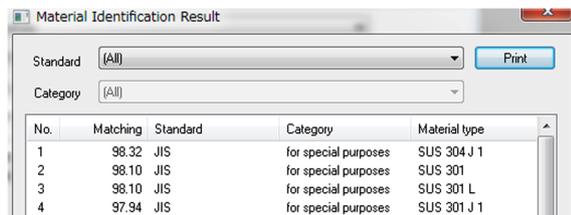


Fig. 16. Results of material identification of the metallic foreign material.

judged to be metal, and a quantitative template was prepared based on “metal.” Table 2 shows the results of SQX analysis.

6. Conclusion

By using EDX spectrometers, foreign material samples can be measured without the need for special settings and sample preparation, which makes them best suited for foreign material analysis, in which analysis time is prioritized. This report has described know-how about and precautions for foreign material analysis using EDX spectrometers. This report has also introduced examples of actual analyses using simulated samples.