# X-ray fluorescence analysis of halogen elements

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## 1. Introduction

Halogen elements correspond to Group 17 in the periodic table and include fluorine (F), chlorine (Cl), bromine (Br) and iodine (I). Materials and products containing halogens are widely used in our daily life. For example, fluorine is contained in Teflon® resin and toothpaste, chlorine is contained in salt and vinyl chloride resin, and bromine is contained in flame retardants in plastics and photosensitizers. While these halogen elements provide useful features to various products, they can also have adverse effects on industries and the environment.

- **Corrosion in production equipment**

If the fuel (oil, refuse derived fuel, etc.) used in an incinerator contains chlorine, it may corrode the combustion furnace and boiler during the production process. Catalysts used in manufacturing processes can be poisoned by chlorine, potentially causing decrease in production efficiency of the target material.

- **Environmental regulations**

Compounds of chlorine and bromine are used as flame retardants for plastics. When plastics containing these elements are incinerated, harmful gases such as dioxins are generated, which may lead to environmental pollution. Recently, halogen-free products and wastes have been promoted due to growing awareness of environmental issues.

- **Countermeasures against defects in semiconductors, electrical devices**

If halogens are contained in organic solvents used in semiconductor manufacturing sites, corrosion and unwanted alteration of electronic components and fine ceramics used as raw materials may occur, degrading functions and performance. Halogen elements in these materials are being analyzed to increase product yield.

For these reasons, halogen elements are analyzed in various industries for acceptance inspection and quality control during manufacturing. Especially in fields where the number of samples to be measured is large, a method capable of quick and easy analysis is required (1).

Combustion-ion chromatography(2),(3) (CIC) and inductively coupled plasma optical emission spectrometry (ICP-OES)(4) are widely used as methods for analyzing halogen elements. However, these methods require complicated sample preparation techniques and equipment maintenance. On the other hand, it is possible to obtain analysis results quickly by using X-ray fluorescence (XRF) spectrometry because sample preparation and instrument maintenance are easy and analyzing time is short. Because of these advantages, XRF is widely used in industries. Examples of the analysis of halogen elements in various samples using XRF are described in this article.

## 2. Bromine Analysis in Plastics by NEX DE (EDXRF)

Recently, recycling of waste plastics has become widespread. Some waste plastics use the Br-containing compound decabromodiphenyl ether (Deca-BDE) as a flame retardant. Since Deca-BDE has an adverse effect on the environment, the production and use of Deca-BDE are prohibited by COP8 of the 2018 POPs Convention (Stockholm Convention on Persistent Organic Pollutants). In this section, an analysis example of bromine in plastic using an energy dispersive (EDXRF) X-ray fluorescence spectrometer Rigaku/NEX DE with direct excitation optics (see Fig. 1 and Table 1) is shown below.

A sample of plastic certified reference material (ERM EC681k) containing Br formed into a disk by hot pressing was used as a measurement sample. Determination of Br was performed using the standardless FP method. The analytical result for Br was 0.8 g/kg, which is in good agreement with the certified value (0.77 g/kg).

Furthermore, the same sample in pellet form (approximate diameter: 3 mm) were analyzed. NEX DE has a camera inside the instrument that can be used to observe the sample to be measured. In addition, NEX DE can be used to analyze samples with variety of forms and sizes, allowing 10, 3, and 1 mm measuring diameters. In this case, the measurement was performed

**Fig. 1.** Rigaku/EDXRF NEX DE.

**Table 1.** NEX DE specifications.

| | |
|---|---|
| X-ray tube | Ag target 12 W |
| Primary beam filter | 6 types + open |
| Diameter | 1, 3, 10 mm |
| Detector | SDD |

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[*] SBU-WDX, X-ray Instrument Division, Rigaku Corporation

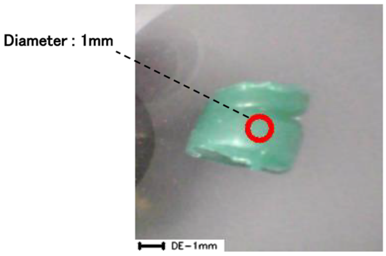

**Fig. 2.** Image of plastic sample taken by NEX DE.

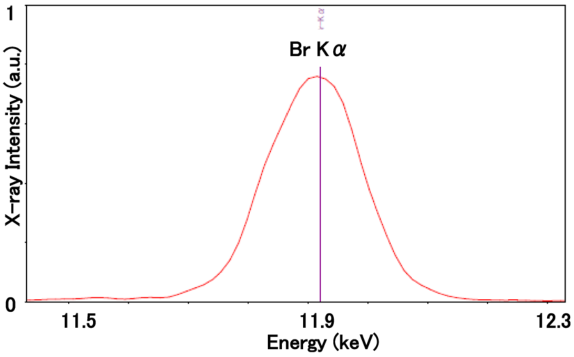

**Fig. 3.** XRF spectrum of bromine in a plastic.

**Fig. 4.** Rigaku/EDXRF spectrometer NEX CG.

**Table 2.** NEX CG specifications.

| | |
|---|---|
| X-ray tube | Pd target 50W |
| Secondary target | For light element, RX9, Cu, Mo, Al |
| Detector | SDD |

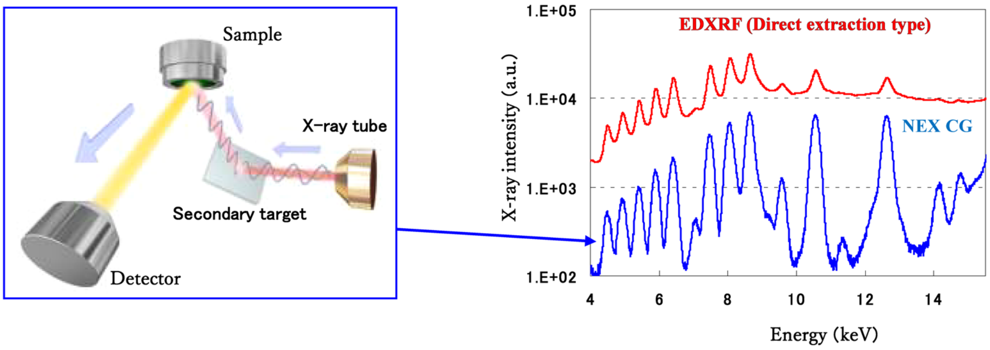

**Fig. 5.** NEX CG optical system and spectrum with NEX CG compared to direct excitation EDXRF.

using a diameter of 1 mm (the area inside the red circle in Fig. 2). Figure 3 shows the spectrum of Br K$\alpha$ line for this sample and the bromine peak can clearly be seen. The analytical result for Br was 0.8 g/kg, which is in good agreement with the certified value 0.77 g/kg. Similar analysis results can be obtained even if the measurement diameter, sample form and size are different. There is almost no interference by peak overlapping in bromine analysis in plastics and good results can be obtained with the EDXRF spectrometer.

## 3. Chlorine Analysis in Liquid Samples

Requirements for the analysis of low concentrations of Cl (ppm level) are increasing because chlorine can cause various defects if contained in certain products. In this section, two analysis examples of Cl contained ppm levels are discussed.

### 3.1. ppm-level chlorine analysis in an organic solvent by NEX CG (EDXRF)

Rigaku/energy dispersive spectrometer NEX CG(5),(6) with Cartesian geometry is shown in Fig. 4. and its specifications are listed in Table 2. Secondary targets and polarized optics are illustrated in the left panel of Fig. 5. The right figure compares the spectrum of an oil sample obtained by a direct excitation type EDXRF spectrometer to the spectrum obtained by the NEX CG. It can be seen that NEX CG has a superior peak-to-background (P/B) ratio, resulting in better detection limits. The monochromatic excitation by the Pd L$\alpha$ line allows ppm-level analysis of Cl, which is difficult to obtain in ICP-OES. An example of analyzing ppm-level Cl contained in an organic solvent is described below.

Sample preparation for liquids in XRF is easy and simple (see Fig. 6). First, cover a sample cup with a thin film (e.g. polypropylene 4.0 $\mu$m). Then, fill the sample cup (polyethylene) with liquid sample (about 4.0 g). Finally, place the sample cup on a position on the sample changer in NEX CG. This sample preparation is not only simple and fast but also very safe for the equipment and operator. Because there is no liquid leakage from the sample container, there is no need to clean the equipment. Also, liquid samples can be measured immediately and continuously.

**Fig. 6.** Organic solvents measured by NEX CG.

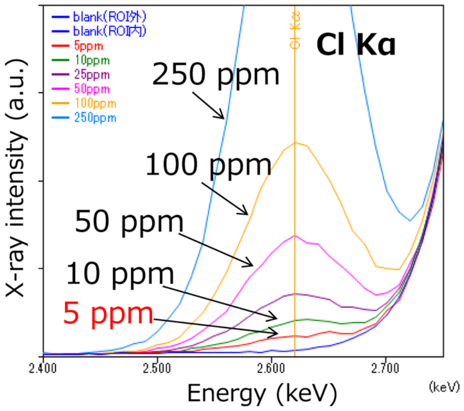

**Fig. 7.** NEX CG XRF spectra of chlorine in organic solvents.

**Fig. 8.** Rigaku/WDXRF spectrometer Supermini200.

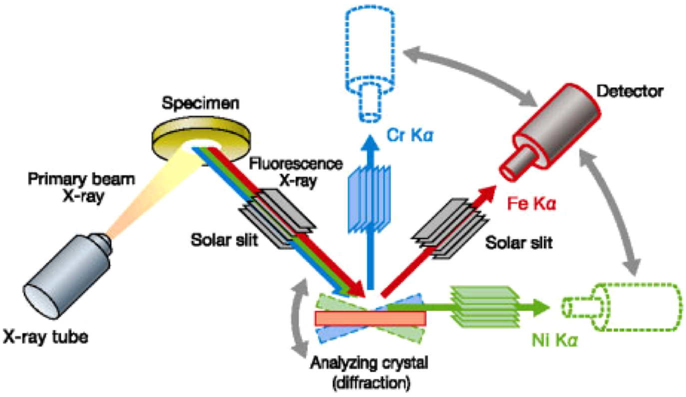

**Fig. 9.** Supermini200 optical configuration.

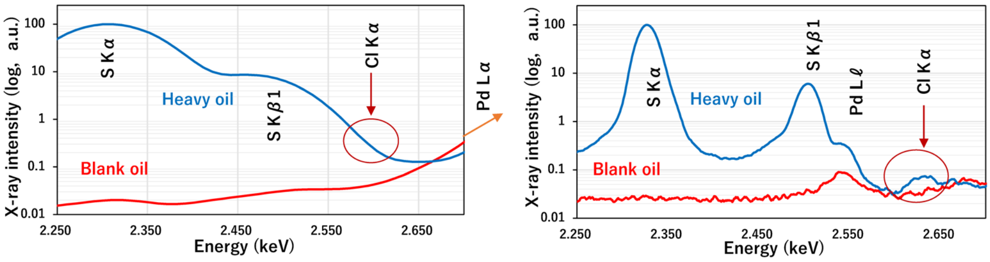

**Fig. 10.** XRF spectra of chlorine in heavy oil (log scale).
Left: NEX CG Right: Supermini200.

Figure 7 shows the spectra of Cl in various organic solvent samples. It detected Cl peaks of not only 250 ppm but also a trace (5 ppm) chlorine peak. Background intensity obtained by general EDXRF with direct excitation is high, so it is difficult to detect 1 ppm level of Cl. On the other hand, low concentration Cl analysis is possible by using a polarizing optical system, such as NEX CG.

### 3.2. Analysis of chlorine below 1 ppm in oils by Supermini200 (WDXRF)

Supermini200 (Fig. 8) is a sequential benchtop wavelength dispersive XRF (WDXRF) spectrometer. WDXRF instruments attain high peak resolution by using the principle of X-ray diffraction from an analyzing crystal (Fig. 9). In this example, Fig. 10 shows the spectra of 10 ppm chlorine in crude oil analyzed by using Supermini200 (WDXRF) and NEX CG (EDXRF). In the spectrum from NEX CG, it is difficult to separate the peaks of Cl from S because crude oil contains a high concentration of S (about to 1.5 mass%) and S K$\beta_1$ interferes with Cl K$\alpha$. On the other hand, the spectrum of the Supermini200 using an analyzing crystal detected the Cl peak and Cl K$\alpha$ peak is clearly separated from giant peak of S K$\beta_1$. Table 3 shows the specifications of the Supermini200 used in the measurements. The RX9 analyzing crystal is highly sensitivities to Cl K$\alpha$. In this section, analysis of Cl below 1 ppm in oils by using Supermini200 is shown.

Cl calibration was set up on the Supermini200 using

**Table 3.** Supermini200 specifications.

| | |
|---|---|
| X-ray tube | Pd target 200 W |
| Analyzing crystal | LiF(200), RX9, RX26 |
| Detector | SC, F-PC |

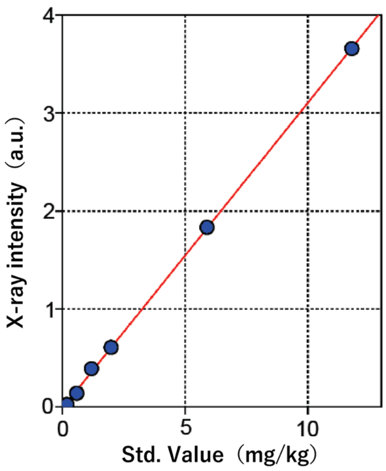

**Fig. 11.** Calibration curve of Cl in oil (Supermini200 with RX9).
Concentration range: 0 to 11 mg/kg (ppm).

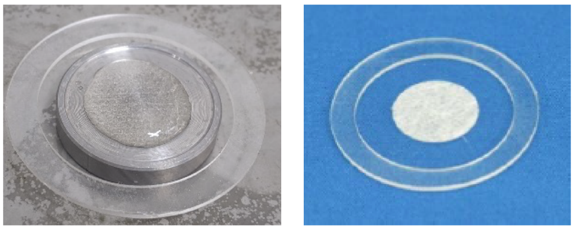

**Fig. 12.** Ultra Carry Light(UCL).
Left: on UCL before drying liquid sample Right: Dried sample on UCL.

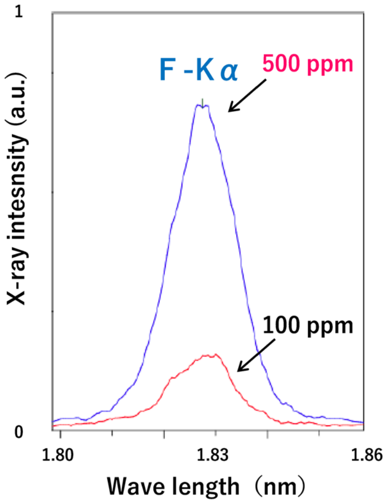

**Fig. 13.** XRF spectra of fluorine in waste fluids.
Blue line: 500 ppm of F Red line: 100 ppm of F.

**Table 4.** Analytical results of F in waste fluid using filter paper method.(unit: ppm).

| Standard value | 500 | 100 |
|---|---|---|
| SQX analysis result | 592 | 142 |

**Fig. 14.** Rigaku/WDXRF spectrometer ZSX Primus IV (left) and ZSX Primus IV*i* (right).

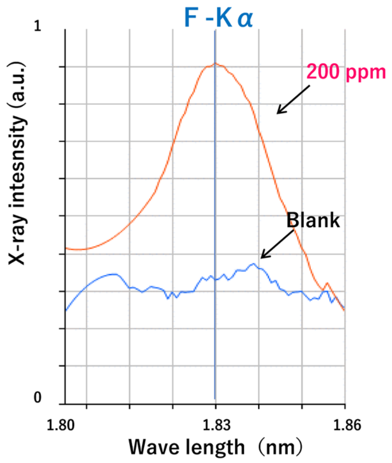

**Fig. 15.** XRF spectra of fluorine in plastic sample.
Red line: F 200 ppm Blue: blank.

the RX9 analyzing crystal. Six calibration samples were prepared by diluting a NIST traceable lubricating oil standard obtained from AccuStandard® (P, S, Cl in white mineral oil, ASTM-P-0121-13). The calibration range is 0 to 11 ppm. The oil samples were prepared as described in section 3.1. The samples were measured for 150 seconds each on the Cl K*α* peak and background. The Cl calibration curve is shown in Fig. 11. The calibration accuracy is 0.1 ppm with a detection limit of 0.1 ppm with the RX9 crystal. Supermini200 allows analysis of Cl well below 1 ppm.

## 4. Fluorine Analysis by WDXRF

Since fluorine's fluorescent X-ray wavelength is longer (lower energy), the detection sensitivity tends to be lower than that of other elements such as Cl and Br; therefore F analysis requires additional techniques for accurate analysis. In this section, two analysis examples of F by WDXRF are shown.

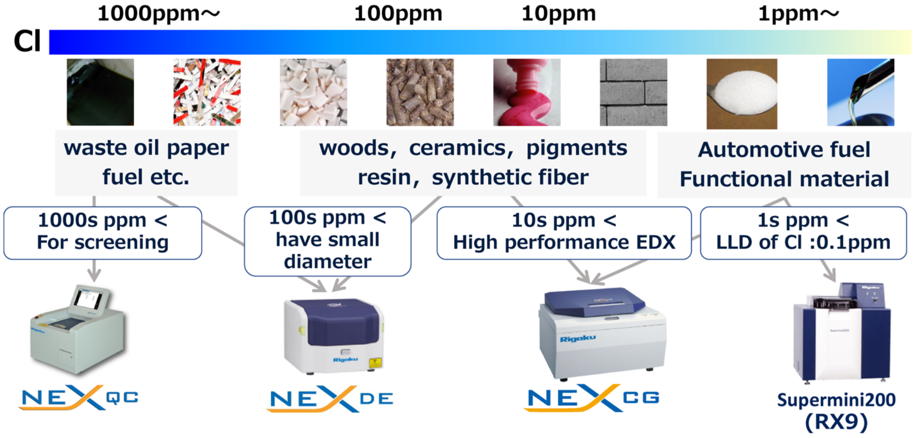

**Fig. 16.** Lineup of XRF spectrometers according to the purpose of analysis for chlorine.

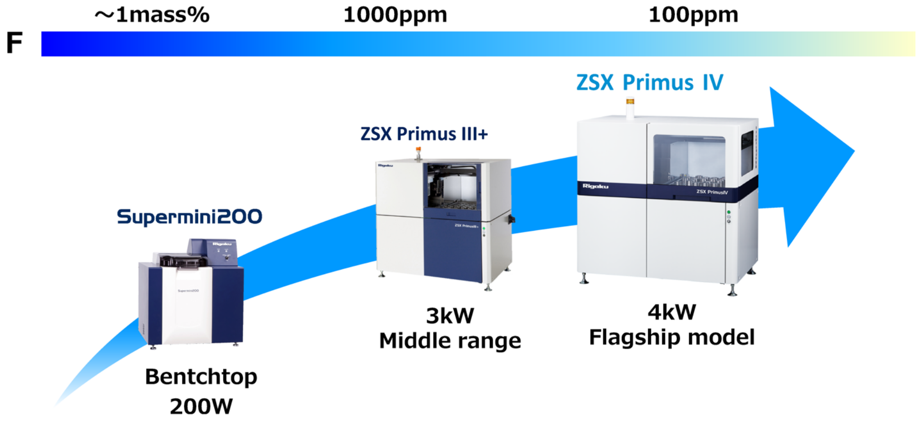

**Fig. 17.** Lineup of XRF spectrometers according to concentration level for fluorine.

### 4.1. Fluorine analysis of ppm level in waste fluids using the filter paper method with Supermini200 (WDXRF)

When measuring a liquid sample directly, a sample film is required to be used. The fluorine fluorescent x-rays can, however, hardly comes through the sample film, which makes analysis of fluorine impossible. On the other hand, sample preparation by the filter method allows analysis of fluorine, because this technique can be carried out without using sample film and can be measured under vacuum atmosphere. In this section, F analysis of ppm levels in waste fluids using the filter paper method (6) by using Supermini200 is shown.

Waste fluids with known F concentrations were pipetted (500 $\mu$L) onto the filter papers of Ultra Carry Light (refer Fig. 12). Figure 13 shows the spectra of F K$\alpha$ in the waste fluids and Table 4 shows SQX analysis results (standardless FP method). Analytical values are in agreement with the standard values. By specifying the pipetted volumes of the fluids, the analysis results can be converted to the concentration in the original liquid.

### 4.2. Fluorine analysis in plastics by ZSX Primus IV and IV*i* (WDXRF)

Rigaku/ZSX Primus IV and IV*i* (7) (Fig. 14) are WDXRF spectrometers equipped with high-power 4 kW X-ray tubes. Fluorine analyses over a wide range, from mass% down to ppm levels can be covered using high power WDXRF spectrometers. In this section, the F analysis results of ppm levels in plastics by using ZSX Primus IV*i* are shown.

Plastic samples with known F concentrations (blank and 200 ppm) were analyzed by using the ZSX Primus IV*i*. The measurements were performed by simply placing the hot-pressed disc specimens in sample holders.

Figure 15 shows F spectra. A fluorine peak can be clearly detected from the 200 ppm sample and the analytical value of SQX analysis was in agreement with the standard value.

### 5. Conclusion

Several application results for controlling halogen elements by XRF were introduced in this article. It was shown that good analysis results can be quickly obtained with Rigaku's lineup of XRF instruments. Sample preparations were simple and easy as well.

### Chlorine analysis

A suitable spectrometer is different depending upon the type of analysis requirement and the analyzing concentration ranges (refer to Fig. 16). For example, NEX QC and NEX DE can be selected when analyzing 1000 ppm level of chlorine contained in waste plastics. These are smaller EDXRF instruments, and they can be installed easily. When analyzing 10 ppm levels in ceramics and pigments, NEX CG equipped with secondary targets and polarized optics is more suitable. And when analyzing low concentrations below 1 ppm in oils, the Supermini200 (RX9 specification) is the most suitable. In addition, high-power WDXRF instruments such as ZSX Primus IV can analyze chlorine from high to low concentrations.

### Fluorine analysis

WDXRF spectrometer is suitable for fluorine analysis. Because fluorescent X-rays of fluorine have a longer wavelength (lower energy), the detection sensitivity tends to be lower than that of other elements such as Cl and Br.

Rigaku has several types of WDXRF spectrometers such as Supermini200 (200 W), ZSX Primus III+(3 kW) and ZSX Primus IV and IV*i* (Fig. 17). Figure 17 shows guideline of selecting suitable spectrometers in concentration ranges to be analyzed. Although the concentration level that needs to be analyzed depends on samples, higher-power WDXRF spectrometers can reach the lowest detection limits.

## Reference

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