Analysis of liquid and powder samples by benchtop wavelength dispersive X-ray fluorescence spectrometer Supermini200 without helium gas

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Abstract

In wavelength dispersive X-ray fluorescence (WDXRF) analysis, liquid and some powder samples are usually measured under helium atmosphere while other samples are measured under vacuum atmosphere. As of 2024, the global shortage of helium gas has resulted in high prices and long delivery times, making analysis using helium gas difficult. Originally, the benchtop WDXRF analyzer Supermini200 measured samples while the sample chamber and optical chamber were either in vacuum or helium atmosphere. Rigaku has developed a new feature for the Supermini200 to measure all forms of samples, including solids, powders, and liquids, without helium gas. This paper describes the details of air/vacuum atmosphere measurement with the Supermini200 and introduces actual analysis examples.

1. Introduction

Recently, helium has been in short supply worldwide(1) due to a decline in the production and increased demand. Because the supply remains low, prices have increased in recent years. In general, WDXRF spectrometers measure samples with the optical path from the sample to the detector in vacuum atmosphere. However, liquid samples cannot be placed in vacuum atmosphere and are therefore typically measured in helium, an inert gas with high X-ray transmittance. In addition, when some fine powders are analyzed without pelletizing by the loose powder method*1, the sample is measured under helium atmosphere because the fine-grained particles are easily scattered when the sample chamber is evacuated and/or ventilated. Liquid samples are one of the most commonly measured materials in X-ray fluorescence analysis, and there are concerns that it may be difficult to continue their analysis due to the uncertain helium supply.

In response to this issue, a new system has been developed for the benchtop WDXRF spectrometer Supermini200 that enables measurement of samples in air atmosphere while maintaining the optical chamber under vacuum. This realizes measurement without helium gas for samples that cannot be measured in vacuum atmosphere. This paper introduces the features of the air/vacuum atmosphere measurement with Supermini200, along with analysis examples.

2. Measurement with Supermini200 without using helium gas

For measurements without using helium gas with Supermini200, a sealing unit that isolates the optical chamber from the sample chamber has been newly developed. By using the sealing unit, the sample chamber can be kept in air atmosphere while maintaining the optical chamber in vacuum (air/vacuum atmosphere measurement). This allows measurements of liquid and powder samples without using helium.

2.1 Sealing unit

For the air/vacuum atmosphere measurement, a sealing unit (a combination of a film support unit and sealing film) between the sample and optical chambers (including the X-ray tube side) is used to maintain the different atmospheric environments. The optical configuration is shown in Fig. 1. Figure 2(a) shows the installed sealing unit viewed from above (sample chamber side). The sealing unit can be easily removed

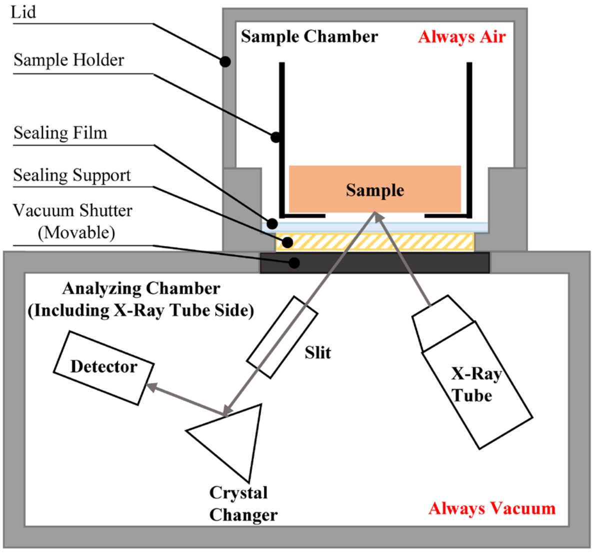

Fig. 1. Optical configuration of the air/vacuum atmosphere measurement.

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[*1] A sample preparation method where loose powder is poured into a sample cell with a film on the measurement side.

by the user and, when detached, measurements can be made in vacuum or helium atmosphere as a conventional Supermini200. Figure 2(b) shows the vacuum shutter closed with the sealing unit removed. In this instrument configuration, when the vacuum shutter is opened during measurement, the optical and sample chambers are under the same atmosphere, and measurements can be performed as usual.

The sealing film is a thin polymer film that deteriorates when exposed to X-rays for a long period of time. Therefore, the sealing film needs to be replaced periodically. To prevent accidents in which the deteriorated film suddenly breaks during measurement, the software monitors the accumulated X-ray exposure time of the sealing film and notifies the user when it is time to replace the film. In addition, the film support unit is made of an X-ray-resistant material to reduce degradation due to X-ray irradiation.

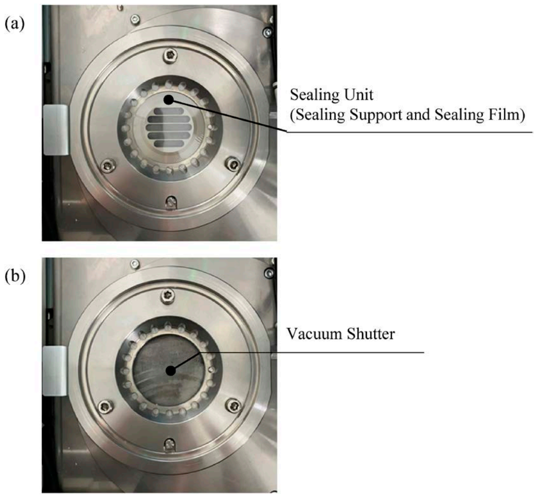


Fig. 2. Sample chamber viewed from above (a) in the air/vacuum atmosphere (b) in the vacuum or helium atmosphere.

2.2 Element line sensitivities in each measurement atmosphere

The Supermini200 has three selectable atmospheres: vacuum, helium, and air/vacuum. In the air/vacuum atmosphere, when the sealing unit is placed in the X-ray path between the sample and detector, the sensitivity will change due to X-ray absorption effects.

Figure 3 shows the intensity ratio of the element lines in each measurement atmosphere relative to vacuum. When the atmosphere in both the analyzing and sample chambers is helium, the intensities of the element lines with higher energy than the Si-K*α* line are almost the same as that of vacuum. In contrast, in air atmosphere, the intensities of the low-energy element lines decrease significantly, and the element lines with lower energy than the Ca-K*α* become difficult to detect.

On the other hand, in the air/vacuum measurement in which the atmosphere in the sample chamber is air while the analyzing chamber is in vacuum, the intensities of the element lines with lower energy than the Zn-K*α* line are greatly enhanced compared to when both the optical and sample chamber have air atmosphere. The intensities of Ca-K*α* to Si-K*α*, which are difficult to detect in the air measurements, are about 60% to 30% relative to vacuum, allowing elements above silicon (Si) to be measured even without helium gas.

2.3 High sensitivity analyzing crystal

Supermini200 can be equipped with up to three analyzing crystals, with standard configurations of LiF(200), PET and RX26. As options, the high sensitivity analyzing crystals RX9 and RX9C for phosphorus (P), sulfur (S), and chlorine (Cl) with low concentrations can be selected in place of PET. These crystal configurations are also compatible with SQX analysis.

Figure 4 shows the qualitative analysis chart of Cl-K*α* when the same sample is measured by PET, RX9, and RX9C, respectively. Compared to PET, the sensitivity of

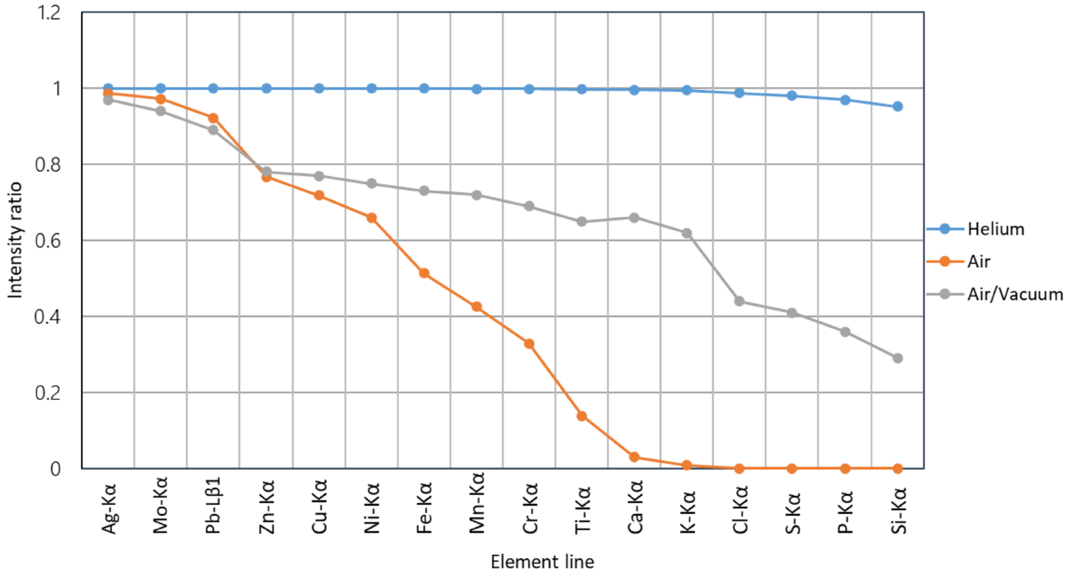


Fig. 3. Intensity ratio of the element lines in each measurement atmosphere relative to vacuum.

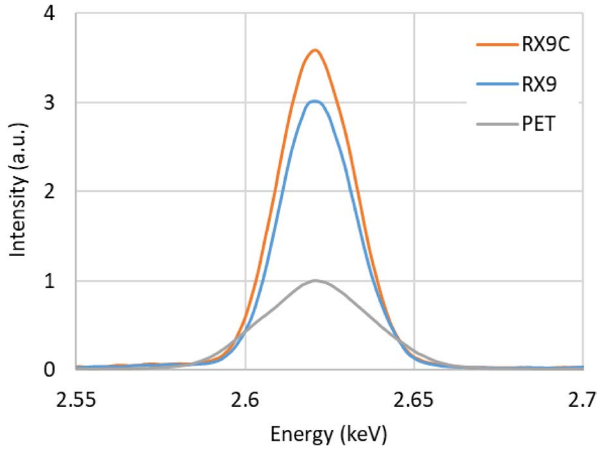


Fig. 4. Qualitative analysis chart of Cl-Kα.

RX9 is about 3 times higher and that of RX9C is about 3.6 times higher. High sensitivity analyzing crystals can compensate for the reduced sensitivity of some light elements in the air/vacuum atmosphere measurements.

3. Applications

The analysis of sulfur and trace chlorine in fuel oil (liquid sample analysis) and the analysis of hazardous elements in petroleum coke (fine-grained powder with loose powder method) are presented as applications of air/vacuum atmosphere measurements. These samples are conventionally measured in a helium atmosphere because they cannot be placed in the vacuum atmosphere.

3.1 Analysis of sulfur and trace chlorine in fuel oil

Sulfur and chlorine contained in petroleum products and oils reduce catalyst performance and produce toxic substances such as sulfur oxides and dioxins during combustion. Therefore, the content of these elements must be controlled. The following is an example of sulfur and chlorine analysis of fuel oil in the air/vacuum atmosphere.

For sample preparation, samples were poured into a sample cell with a sample film as a measurement window (Fig. 5) and covered with a cap. After preparation, six calibration samples were measured with a Supermini200 to generate calibration curves for sulfur and chlorine (Fig. 6). The accuracy of each calibration curve was satisfactory, with 58 ppm (concentration range ～10,000 ppm) for sulfur and 0.98 ppm (concentration range ～50 ppm) for chlorine.

The analytical line Cl-Kα (2.622 keV) is close to the S-Kβ1 line (2.464 keV). WDXRF has superior spectral resolution and can detect these lines separately on samples containing both sulfur and chlorine. On the other hand, because energy dispersive X-ray fluorescence (EDXRF) cannot distinguish these lines, it is difficult to analyze trace amounts of chlorine by EDXRF. Therefore, WDXRF is recommended for more accurate analysis of trace amounts of chlorine in fuel oil.

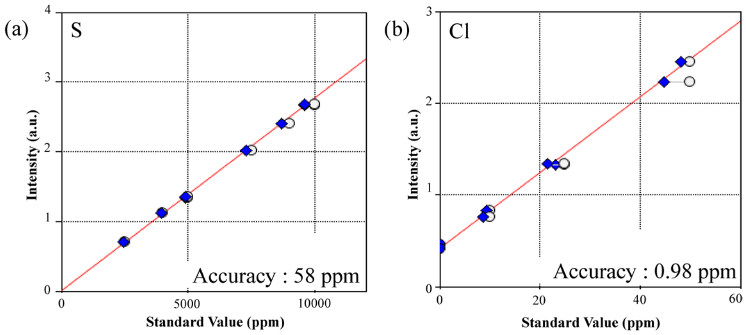
The air/vacuum measurements of the Supermini200 comply with the standard test method ASTM D2622(2) for sulfur in petroleum products by WDXRF analysis.

3.2 Analysis of hazardous elements in petroleum coke

Petroleum coke, the final residue of the oil refining process, is used as fuel after desulfurization, but the content of hazardous elements must be controlled for environmental protection. Petroleum coke is usually measured by the loose powder method because of its fine-grained particles and difficulty in pelletizing. When a fine powder sample prepared by the loose powder method is measured in a vacuum atmosphere, the sample

Sample weight : 4 g
Sample cell : 3399N095
Sample film : Mylar 3.6 μm

Fig. 5. Fuel oil sample after sample preparation.



Crystal : RX9C
Detector : F-PC
Measuring time : Peak 10 sec. , BG 10 sec.

Crystal : RX9C
Detector : F-PC
Measuring time : Peak 40 sec. , BG 40 sec.

Fig. 6. Calibration curves for each component in fuel oil (a) sulfur (b) chlorine

Sample weight : 4 g
Sample cell : 399N095
Sample film : Prolene 4 µm

Fig. 7. Petroleum coke sample after sample preparation.

may be scattered during sample chamber evacuation and/or ventilation. The following is an example of the analysis of hazardous elements in petroleum coke in the air/vacuum atmosphere.

For sample preparation, petroleum coke powder was placed in a sample cell with a sample film as a measurement window (Fig. 7) and covered with a cap. Six calibration samples were prepared and measured with a Supermini200 to generate calibration curves for five elements: sulfur, calcium, vanadium, iron, and nickel (Fig. 8).

The accuracy of each calibration curve was satisfactory: 490 ppm for sulfur (concentration range ～50,000 ppm), 16 ppm for calcium (concentration range ～1000 ppm), 9.3 ppm for vanadium (concentration range ～600 ppm), 190 ppm for iron (concentration range ～7000 ppm), and 34 ppm for nickel (concentration range ～250 ppm).

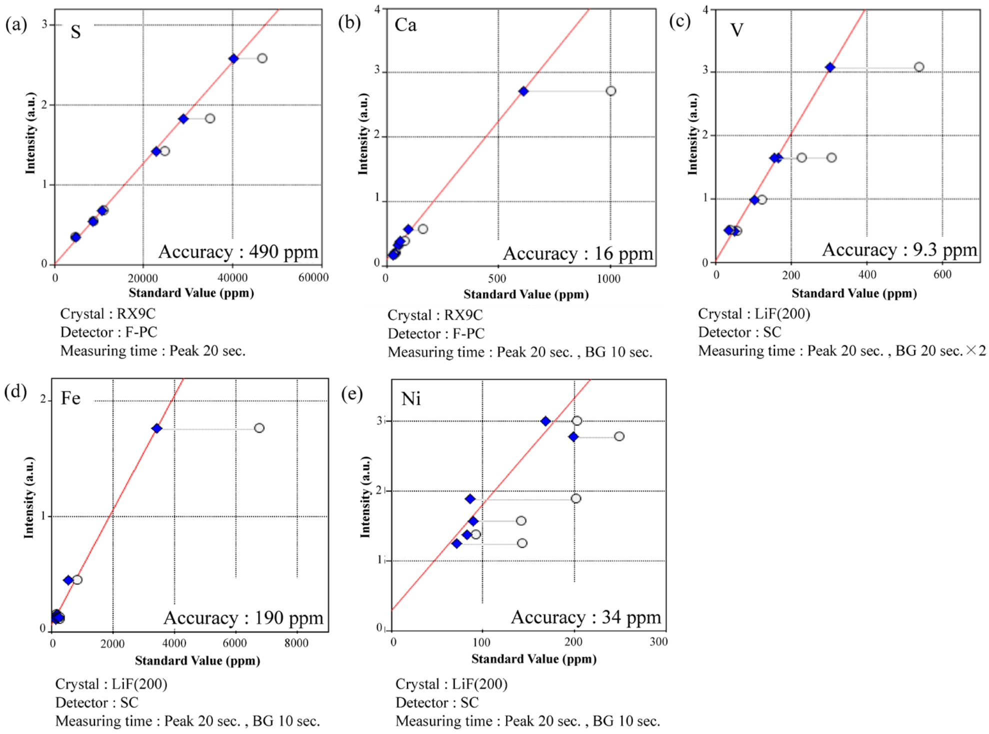
4. Summary

Rigaku has developed a new air/vacuum measurement system for the Supermini200. Although the range of elements to be quantified in the air/vacuum atmosphere measurement is limited from silicon to heavier elements, all forms of samples such as solids, powders, and liquids can be measured without helium gas. Since measurement in vacuum and helium atmosphere is also possible as usual, helium gas consumption can be reduced by selecting the measurement atmosphere according to the sample condition and elements to be analyzed, resulting in lower running costs in lab operation.

References

(1) "Helium prices surge to record levels as shortage continues", *Physics Today*, Volume 33, Issue 9, September 2023.

(2) ASTM D2622-21, Standard Test Method for Sulfur in Petroleum Products by Wavelength Dispersive X-ray Fluorescence Spectrometry, ASTM International (2021)



(a) Crystal : RX9C
Detector : F-PC
Measuring time : Peak 20 sec.

(b) Crystal : RX9C
Detector : F-PC
Measuring time : Peak 20 sec. , BG 10 sec.

(c) Crystal : LiF(200)
Detector : SC
Measuring time : Peak 20 sec. , BG 20 sec.×2

(d) Crystal : LiF(200)
Detector : SC
Measuring time : Peak 20 sec. , BG 10 sec.

(e) Crystal : LiF(200)
Detector : SC
Measuring time : Peak 20 sec. , BG 10 sec.

Fig. 8. Calibration curves for each component in petroleum coke (a) sulfur (b) calcium (c) vanadium (d) iron (e) nickel.