X-ray fluorescence analysis of liquid samples without helium gas

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Abstract

Helium gas is becoming more difficult to obtain these days due to decreased supply and increased demand. In X-ray fluorescence analysis, helium gas is often used in the analysis of liquid samples, while processing samples as solids is possible under a vacuum. In this article we introduce two liquid sample processing methods for measurements under a vacuum: the droplet method and the oil solidification method. In the droplet method a solution sample is dropped onto a filter paper and dried, and in the oil solidification method an oil sample is mixed with a solidifying agent and solidified.

1. Introduction

Helium gas continues to be difficult to obtain due to decreased supply and increased demand. When a liquid sample is measured by X-ray fluorescence analysis, helium gas is required if the sample is measured in its liquid state. However, if a liquid sample is converted to a solid by sample processing, it can be measured under a vacuum. The droplet method, in which a sample is dropped onto filter paper and dried, is effective for solution samples. The oil solidification method, in which the sample is mixed with a solidifying agent and solidified, is effective for oil samples.

This article describes sample preparation procedures, appropriate sample types, and precautions for analysis using the droplet method and the oil solidification method for wavelength dispersive X-ray fluorescence (WDXRF) spectrometers.

2. Background

As of 2022, the helium supply decrease can be attributed to the fact that helium gas refinery plants have been out of operation for some time due to breakdowns or periodic inspections, and congestion in global container shipping and rising transportation costs have caused disruptions in logistics[(1)]. On the other hand, the demand for helium has been increasing due to the expansion of the optical fiber and semiconductor industries, and there still is a market shortage of helium because the supply cannot keep up.

The shortage of helium gas also affects X-ray fluorescence analysis. In WDXRF analyzers, samples are generally analyzed under a vacuum. Liquid samples, however, are measured by replacing the vacuum inside the instrument with helium. No alternative gas is fully compatible with helium in terms of high X-ray transmittance and stability. Therefore, if helium gas is not available, it is difficult to analyze liquid samples as they are.

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3. Sample Processing Method for Measuring Liquid Samples in Vacuum

Figure 1 shows analysis methods for liquid samples. Many applications need helium gas for measurement, such as concentration and/or additive/impurity control analysis of plating solutions, component control of crude oil and heavy oil, sulfur analysis in fuel oil, and analysis of additive elements and wear metal powder in lubricating oil. The liquid method is mainly used for these measurements, in which a liquid sample is poured into a sample cell.

In order to perform measurements in a vacuum, the sample must be prepared as a solid, not a liquid. As preparation methods for measurements in a vacuum, the droplet method is effective for solution samples and the oil solidification method is effective for oil samples.

4. Droplet Method

In the droplet method, a constant amount of liquid sample is dropped onto filter paper and the dried filter paper sample is measured[(2)]. Advantages of the droplet method are: 1) measurements can be performed in a vacuum, 2) high sensitivity of measurements of light elements (Na, Mg) because X-ray fluorescence is detected without a sample film unlike the liquid method, 3) preparation with only a small amount of sample (several hundred μL), and 4) measurements without concern for splashing of solution during measurements.

4.1. Micro Carry and Ultra Carry overview

Commercially available filter paper can be used, but Rigaku's special filter paper (Micro Carry) with

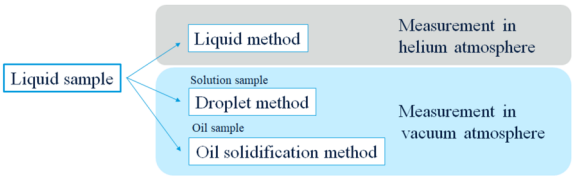

Fig. 1. Analysis methods for liquid samples.

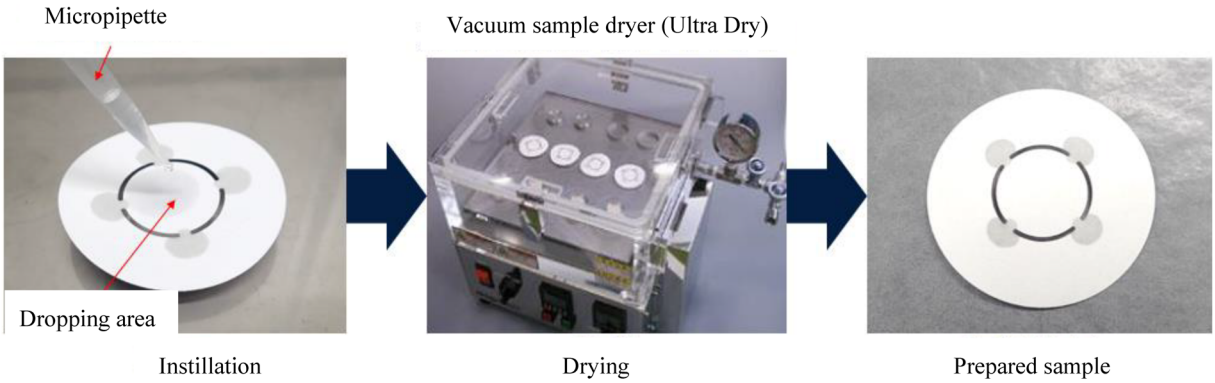

Fig. 2. Sample preparation procedure for the droplet method.

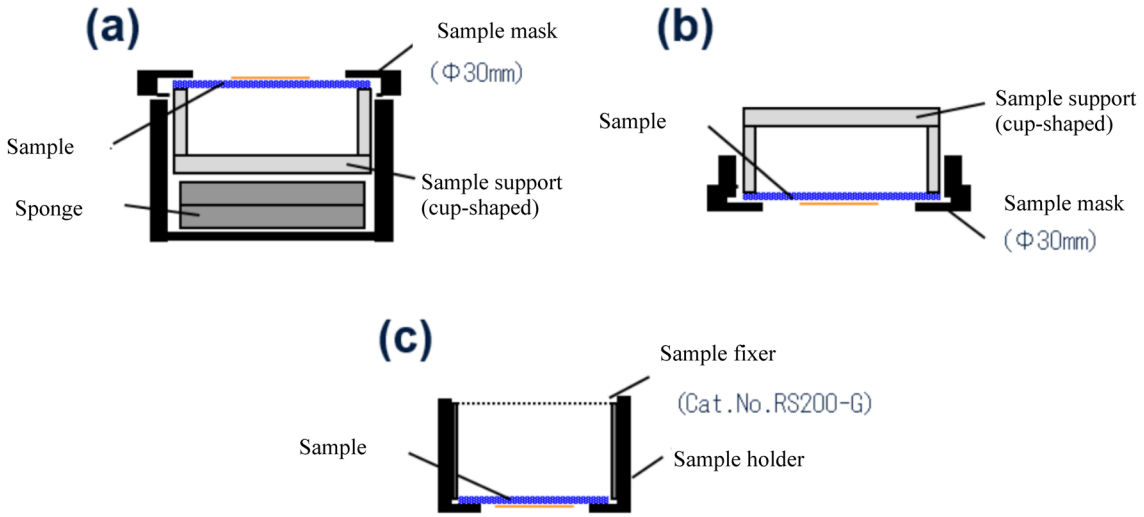

Fig. 3. Installation of filter paper samples ((a) Tube-above type instrument (ZSX Primus II, ZSX PrimusIII+, ZSX Primus IV etc.), (b) Tube-below type instruments. (ZSX Primus, ZSX Primus IVi, etc.), (c) Benchtop tube-below type instruments (Supermini200 etc.)).

anti-diffusion slit enables quantitative analysis by instillation of a constant amount. High-sensitivity filter paper (Ultra Carry, Ultra Carry Light) with an instillation spot for more sensitive measurement of aqueous solution samples, is also available. This article describes the preparation procedure using Micro Carry as an example. Ultra Carry can be used for preparations with the same procedure.

4.2. Preparation procedure

The preparation procedure for Micro Carry is described below (Fig. 2). First, prepare a clean table, and place a ring so the filter paper does not directly touch the table. The filter paper is placed on the ring and a certain amount of sample is dropped into the central spot area using a micropipette. The recommended drop volume is 50–100 μL for Micro Carry and 50–500 μL for Ultra Carry®. After instillation, the filter paper must be dried thoroughly before measurement. Natural drying is acceptable, but heating at a constant temperature of 40–60°C (104–140°F) enables quicker drying. A sample can be dried in about 30 minutes by low-temperature heating and vacuum drying using a vacuum sample dryer (Ultra Dry). Since filter paper samples are thin and easily penetrated by X-rays, cup-shaped sample supports and sample fixtures are used for measurements to prevent the detection of the unconcerned rays from the sample support or plate-shaped sample support. Figure 3 shows a diagram of the installation of filter paper samples into instruments.

4.3. Example of a droplet method measurement

Figure 4 shows qualitative analysis charts as an example of actual measurements. The samples were prepared from a standard solution containing 23 elements with 100 ppm each. Measurements were performed with ZSX Primus IVi (tube wattage: 3 kW). The qualitative analysis chart for the liquid method is also shown for comparison. The droplet method has a high peak-to-background ratio, making it easy to detect trace component peaks. Moreover, light elements such as Na and Mg can also be measured because no film is used during measurement.

Calibration curves were prepared for Mg, Al, Cu, and Zn in solution using a standard sample containing 23 elements, and the lower limits of detection were

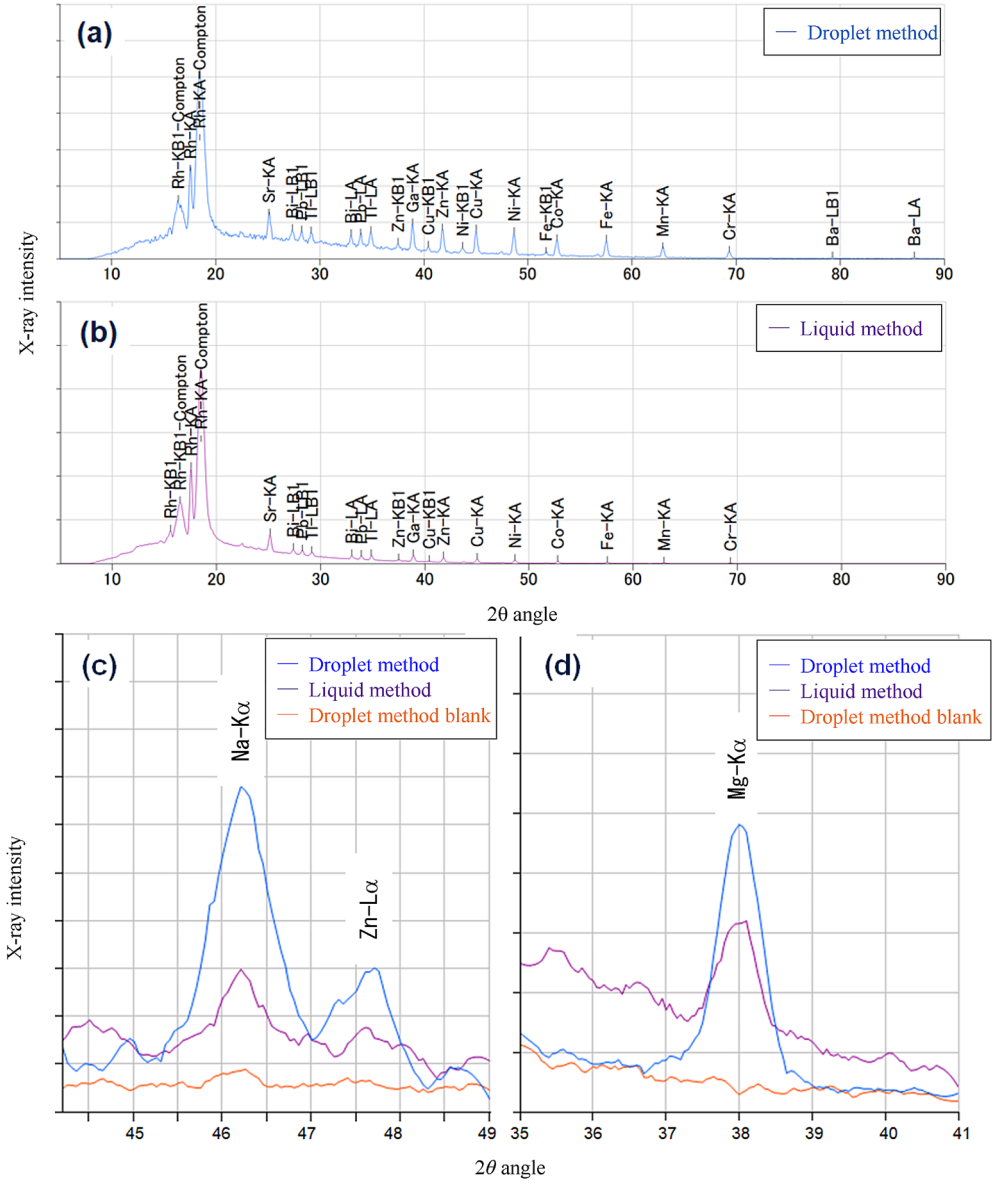

Fig. 4. The qualitative analysis charts of samples prepared by the spot and liquid methods (a) (b) Ti to Cm, (c) Na-Kα, (d) Mg-Kα.

calculated (Table 1). Measurements were performed with ZSX Primus IVi (tube wattage: 2.4 kW). The measurement time conditions were as follows: 40 seconds for peak and 10 seconds for background measurements for Mg, Al, and Cu, and 40 seconds for peak without a background measurements for Zn. Detection limits for the liquid method are also shown for comparison. The droplet method can determine light elements such as Mg with higher sensitivity than the liquid method because no measurement film is used.

Table 1. Comparison of lower detection limits of the droplet and liquid methods.

Element	Droplet method (ppm)	Liquid method (ppm)
Mg	0.5	3.4
Al	0.3	0.9
Cu	0.2	0.2
Zn	0.2	0.2

4.4. Precaution for droplet method

The droplet method is mainly used for the analysis of aqueous solution samples in which the solvent evaporates completely. This method is not suitable for highly concentrated solutions that form crystals after drying. For samples containing solutes at high concentrations, such as plating solutions, it is necessary to dilute the sample approximately 20 times before sample preparation. This method is not suitable for solutions with low surface tension, such as interfacial active agents and organic solvents, because of the difficulty of sample processing. Since the density in the spot area of the filter paper may be uneven depending on the concentration of the components in the sample, it is necessary to pay attention to the concentration and drop volume so that the components are dispersed homogeneously.

5. Oil Solidification Method

In the oil solidification method, oil samples are mixed with an oil solidifier, dissolved, and then solidified[3]. Advantages of the oil solidification method include: 1) measurement in a vacuum atmosphere, 2) no sedimentation of metal powder or other components in the lubricating oil during measurements, and 3) high-sensitivity analysis of light elements because some samples can be measured without a sample film.

At Rigaku, we mainly use 12-hydroxystearic acid, which has few impurities, as an oil solidifier (Fig. 5). The melting point is 90°C (194°F) and the boiling point is 180°C (356°F). The oil solidification method is applicable to samples such as lubricating oil and grease.

Fig. 5. Oil solidifier supplied by Rigaku (Cat. No. 3399H301).

5.1. Preparation procedure

The preparation procedure for the oil solidification method is described below (see Fig. 6). First, the oil sample and oil solidifier are weighed and placed in a screw vial. Oil sample : solidifier = 1 : 1 (2.5 g : 2.5 g) is common. The cap of the screw vial is loosely closed, and then the sample and solidifier are heated for approximately 15 minutes at 80 to 160°C (176 to 320°F), depending on the temperature characteristics of the sample and solidifier, until completely liquefied. Care must be taken to ensure that the heating temperature does not exceed the flash point or spontaneous ignition point of the mixture. Once the sample and liquefied solidifier are completely mixed, molding is performed. Al rings for pressure molding of

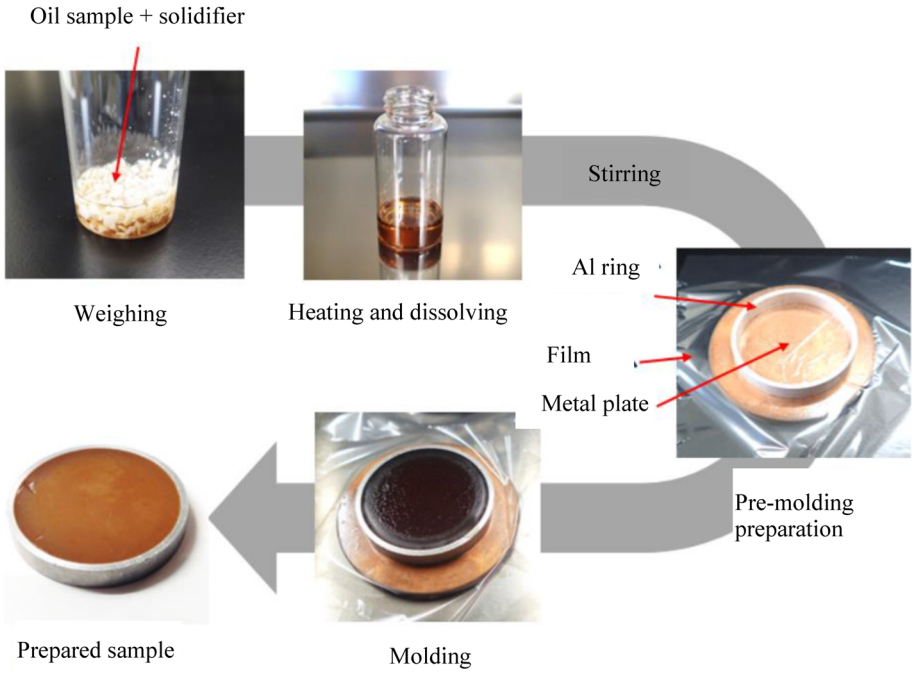

Fig. 6. Preparation procedure of the oil solidification method.

Table 2. SQX analysis values of oil solidification and liquid methods (Unit: ppm).

	Na	Mg	Al	Si	P	Ca	Ti	V
Oil solidification method	101	101	105	105	88	89	96	97
Liquid method	—	101	94	95	97	95	95	98

	Cr	Mn	Fe	Ni	Cu	Zn	Pb
Oil solidification method	102	92	106	98	92	89	72
Liquid method	101	101	102	100	96	93	94

powder samples or sample cells are used as molds. A highly heat-resistant sample film, such as polypropylene or polyimide, is laid on a metal plate with high thermal conductivity, a mold is placed on top of the film, and the liquefied sample is poured all at once. Since the surface that is in contact with the film is the measurement surface, the film must be flat during cooling. Sample processing is finished when the entire sample has cooled.

5.2. Example of a measurement using the oil solidification method

SQX analysis (standardless FP analysis) of elements in oil is introduced as an example of a measurement using the oil solidification method (Table 2). SQX analysis is also suitable for oil solidified samples. The analysis results can be calculated as the content rate in the oil by inputting the solidifier, dilution ratio, and sample weight. The sample is an oil standard sample containing 21 elements at 100 ppm each. Measurements were performed with ZSX Primus IVi (tube wattage: 3 kW). Results from the liquid method SQX analysis are also shown for comparison.

Although in the oil solidification method a sample is diluted with a solidifier, it allows measuring light elements such as Na with higher sensitivity than the liquid method because it does not use a thin film during measurement.

5.3. Precaution for oil solidification method

Oil with high water content is not suitable for the oil solidification method because it separates from the solidifier and does not solidify. Highly volatile samples such as fuel oil are also not suitable because the sample may volatilize during the heating process. Analysis errors may also occur for samples whose volume decreases due to volatilization of components during storage at room temperature after sample preparation.

6. Summary

This article describes two analysis methods for liquid samples that do not use helium gas. The liquid method requires helium gas; however, some liquid samples can be processed as solids using the droplet method or the oil solidification method, which enable measurements under a vacuum. Confirming the applicable sample types and concentration ranges and replacing the conventional liquid method of analysis with these methods allows a significant decrease in the use of helium gas. The details of each sample preparation can be found in the reference articles[2, 3]. It is important to determine the appropriate conditions for the purpose of the analysis after a thorough preliminary consideration.

References

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