Sample preparation for X-ray fluorescence analysis VIII. Liquid solidification method

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1. Introduction

Sample preparation by liquid and droplet methods have been discussed in the previous installment of "Sample preparation for XRF analysis". In this issue, a novel preparation method by which liquid samples are solidified is described. Solidifying samples such as lubricating oils allows measurement to be performed in vacuum instead of helium and without the need of sample films. This is especially advantageous for the measurement of light elements which have poor X-ray transmission rates through helium atmosphere and films. Another benefit of the solidification method is prevention of particle settlement such as wear metals in used oils during measurement.

Sample preparation is performed by mixing the liquid sample with a solidifier, a material that is solid at room temperature but liquefies when heated. The well mixed heated liquid is then cooled down to form a solidified specimen. Due to the heating process, volatile liquids are not suitable for measurement by solidification. Once the sample is solidified, the original pure liquid cannot be isolated and therefore the method is technically a "destructive technique".

This article describes the sample preparation procedure, suitable sample types, application examples and other considerations for analysis by solidification method with a wavelength dispersive X-ray fluorescent (WDXRF) spectrometer.

2. Sample preparation

The sample preparation procedure is illustrated in Fig. 1. First, the liquid sample and solidifier are carefully weighed and placed in a vial. Typical sample to solidifier ratio is 1 : 1 (2.5 g : 2.5 g). Loosely cap vial and heat at 80–160°C depending on sample and solidifier characteristics until completely liquefied (about 15 minutes). Minimum heating temperature is determined by the melting point of the solidifier. Most importantly for safety reasons, the applied temperature must not exceed the mixture's flash point or autoignition temperature.

The solidifier supplied by Rigaku (Cat. No. 3399H301) is shown in Fig. 2. It is a low impurity 12-hydroxystearic acid ($C_{18}H_{36}O_3$) with 90°C melting and 180°C boiling point. Other solidifiers such as reagent grade paraffin wax can be used but generally have a lower melting point of below 60°C. This requires covering sample with film for measurement since it can warm up and begin to liquefy when irradiated by X-rays inside the spectrometer. Low melting point solidifiers can still be effective however in preventing settling of particles in the liquid. When measurement is performed with film, sample to solidifier ratio can be increased to for example 10 to 1. Sample to solidifier ratio can also be optimized depending on melting point of the sample.

Solidifiers are typically supplied as shaved chips or solid blocks, but can easily be finely ground with

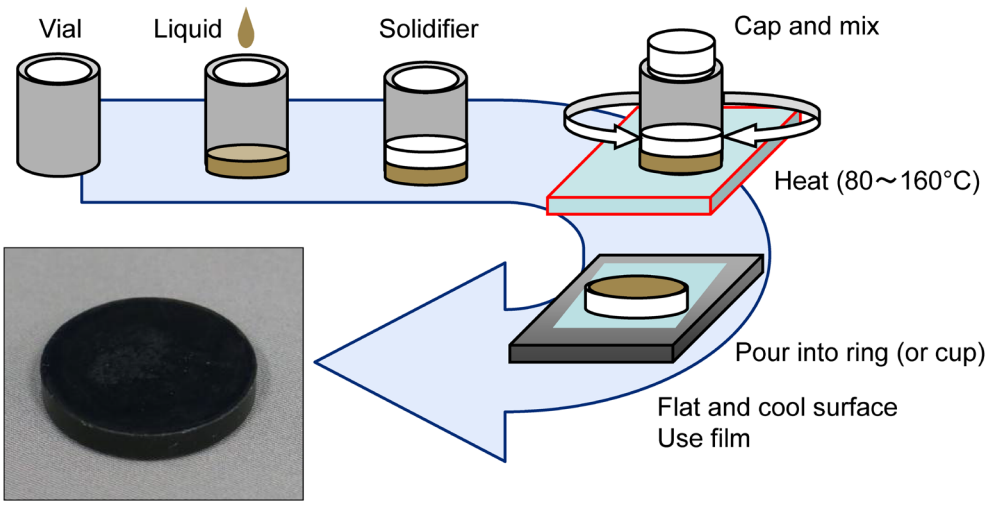

Fig. 1. Sample preparation for solidification method.

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Fig. 2. Solidifier supplied by Rigaku (Cat. No. 3399H301).

a mortar and pestle. Preparing such finely ground solidifier can be useful to accurately and precisely fine-tune the final sample to solidifier weight ratio. Since solidifiers absorb almost no moisture, storing in a typical laboratory vial is sufficient.

After thoroughly mixing the sample and liquefied solidifier, pour the mixture into a mould such as for example a briquetting ring or sample cup. Cover the surface on which the mould is placed with a tightly fixed sheet of film such as polypropylene to allow consistent specimen removal without damaging specimen surface. The film should remain taut and even throughout the cooling process since specimen surface in contact with the film is the measurement side. Using a pre-cooled flat object with high thermal conductivity facilitates solidification.

3. Sample characteristics and measurement considerations

Suitability of sample preparation and measurement by solidification method depends on the sample's initial boiling point (IBP). Since IBP depends on pressure, the measurement atmosphere needs to be selected carefully to minimize potential contamination of the spectrometer's optical path by the sample during measurement. Amount of sample volatilization during solidifier liquefaction and solubility with the solidifier also play a role in method feasibility.

3.1. Lubricating oils and greases

Solidified lubricating oils and greases can be measured in vacuum atmosphere without sample film due to having a relatively high IBP of 265°C under normal atmospheric pressure. This temperature corresponds to an IBP of about 40°C under typical vacuum atmosphere measurement. A small amount of vaporization may occur during measurement but effect on spectrometer is negligible since these components are quickly removed by the vacuum pump.

3.2. Heavy and light crude oils

Heavy and light crude oils tend to contain components with IBP below 265°C and therefore routine measurement of such solidified samples in vacuum

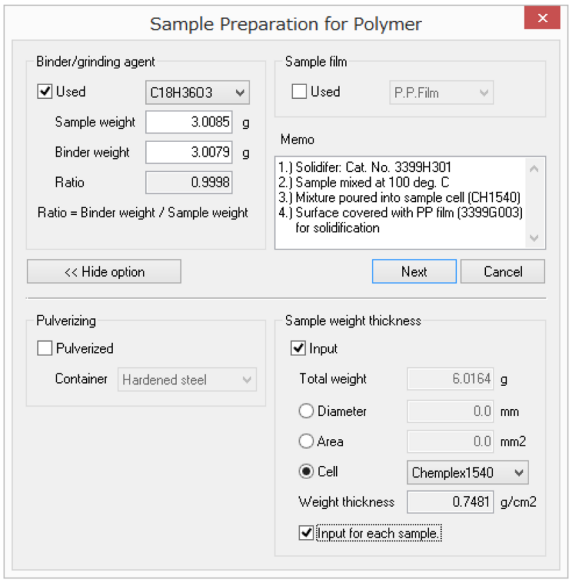

Fig. 3. Qualitative application setting for SQX analysis of a solidified sample.

should be avoided. Measurement in helium atmosphere keeps the IBP high enough preventing any spectrometer contamination. Measurement in vacuum with sample covered with film is another option.

3.3. Samples not suited for solidification method

Samples with low IBPs such as kerosene, gasoline and diesel fuels are not suited for solidification method since sample will evaporate during melting of the solidifier. Liquids that contain H_2O are also not suited since the sample does not mix well with the solidifier.

4. Application examples

4.1. Semi-quantitative (SQX) analysis

To accurately perform SQX analysis of a solidified sample, several specific settings in the software are required. To account for the sample being "diluted" by the solidifier, first create a new entry for $C_{18}H_{36}O_3$ in the compound table as compound type "Binder". Then, create a polymer qualitative application. In the "Sample Preparation" setting, select $C_{18}H_{36}O_3$ as binder and enter the sample and binder (solidifier) weights. This allows the SQX calculation to take the dilution of original sample by the solidifier into account. In addition, since the solidified sample matrix is very light, sample may not have infinite thickness for high energy measurement lines and therefore setting sample thickness is recommended. This takes sample thickness into account when calculating concentrations.

The dialog box in Fig. 3 shows sample preparation setting in the ZSX software for a polymer qualitative application for measurement of a solidified sample. The liquefied mixture was solidified in a Chemplex® CH1540 sample cell. When a different mould is used, set either the actual diameter or area of the prepared sample, not the measurement diameter or area. By selecting "Input for each sample", the variations in

Table 1. SQX analysis result of a solidified oil standard sample (each element 500 ppm).

Unit: ppm

	Solidification	Liquid		Solidification	Liquid
Na	509	—	Fe	515	504
Mg	490	505	Ni	501	506
Al	501	507	Cu	510	491
Si	510	519	Zn	480	461
P	480	473	Mo	505	488
Ca	460	443	Ag	486	470
Ti	475	479	Cd	455	460
V	483	474	Ba	532	543
Cr	540	539	Pb	520	505
Mn	523	520			

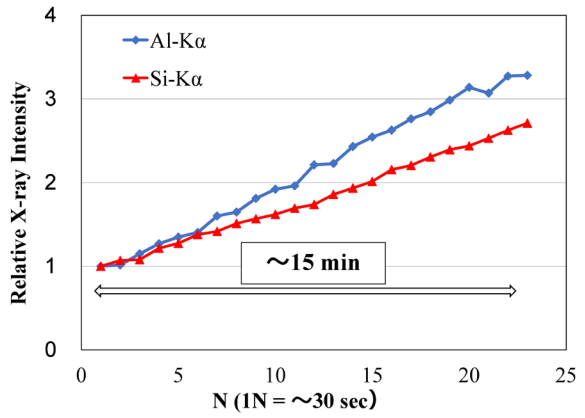

Fig. 4. Repeat X-ray intensity measurement of Al and Si in slurry oil.

sample and solidifier weights between specimens can be compensated given the weights are known. Be sure to set the base component of the liquid sample, for example CH_2 for typical oils, as balance component in the "Parameters" dialog box.

Table 1 shows SQX analysis result of an oil standard sample with multiple elements each at 500 ppm. For comparison, analysis result by direct liquid method (liquid sample covered with film, measured in helium) is shown. For both preparation methods, CH_2 was set as balance component to calculate concentrations. Results show that solidification method allows accurate analysis comparable to direct liquid method with the added advantage of being able to analyze Na since sample is not covered with analysis film and measurement can be performed in vacuum.

4.2. Prevention of particle settling

Slurry oil (aka decant oil) contain suspended solids known as catalyst fines. Figure 4 shows change in Al-Kα and Si-Kα intensity of such a sample by direct liquid method. Due to the settling of particles, the intensities increase over time making measurement of "correct" X-ray intensity difficult.

Repeat analysis result of a solidified slurry oil sample is shown in Table 2. Settling of particles is prevented and analysis results are stable over time. It should be noted that sample preparation reproducibility highly depends on how consistently the specimen can be sampled. Slurry oils with catalyst fines several 100 ppm and higher and depending on particle size distribution can be very difficult to sample consistently leading to poor sample preparation reproducibility.

Table 2. Repeat analysis of Al and Si in a solidified slurry oil sample.

Unit: ppm

Run	Al	Si
N=1	19	21
2	21	22
3	20	25
4	22	22
5	19	26
6	22	25
7	21	22
8	22	24
9	23	22
10	20	24
Average	20.9	23.3
Std. Dev.	1.37	1.70
Maximum	23	26
Minimum	19	21
Range	4	5

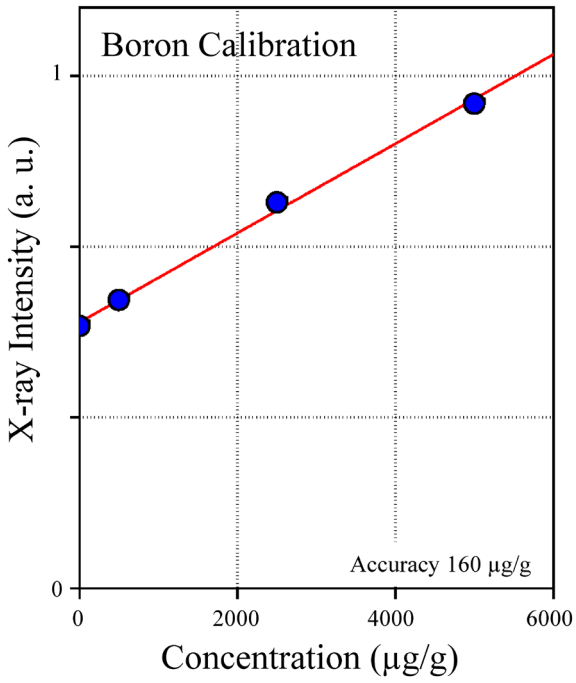

Fig. 5. Boron calibration of solidified oil standard samples.

4.3. Quantification of ultralight elements in oil

A 5000 μg/g boron standard oil sample supplied by

VHG Labs and a blank oil sample were used to prepare calibration samples from 0 to 5000 μg/g. Samples were solidified and boron calibration was set up as shown in Fig. 5. Measurement was performed in vacuum and without film, allowing measurement of ultralight elements in oil.

5. Summary

Sample preparation of liquids by solidification method has been described. Advantages of the solidification method are ability to measure samples in vacuum and without film for light element analysis. It is also effective in preventing settlement of particulates in the sample during measurement. Suitable sample types for solidification method depends on the IBP of the sample. Liquids that contain water are not suitable since such samples are not miscible with the solidifier. Application examples demonstrating ability to analyze light elements not possible by direct liquid method and effectiveness to prevent particle settlement have been shown. For certain application requirements, liquid solidification method is a viable alternative.

References

(1) T. Moriyama and A. Morikawa: *Rigaku Journal (English version)*, **33** (2017), No. 1, 24−29.

(2) J. H. Gary, G. E. Handwerk and M. J. Kaiser: *Petroleum Refining—Technology and Economics*, *Fifth Edition*, CRC Press, (2007).