XRF analysis of liquids using sample cups and films

Introduction

The preparation of liquids using X-ray fluorescence analysis is done by simply pouring the sample into a sample cup.

Analysing in sample cups allows for easy and versatile analysis of liquids, but also powders. However, careful sample preparation is required for reliable results and safe operation of the XRF instrument.

Liquids should only be measured in flawless, correctly prepared cuvettes with undamaged measuring foils. Before the analyses, a short waiting time is recommended to check the tightness of the sample cup. Measuring foils and sample cups are designed as disposable material and should be replaced after each measurement.

To protect the XRF system from contamination, measurements of liquids or loose powders in cuvettes are not typically performed under vacuum. Instead, the analysis is usually carried out under a helium atmosphere. Many modern EDXRF systems also allow measurements in air or nitrogen, depending on the application.

If these recommendations are followed, sample cup measurements can be carried out safely, reproducibly and with high analytical quality.

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Available sample cups and types of film

Many different sample cup types are available and can be used depending on the instrument's holder type. You can find a list of available sample cups here:

https://www.fluxana.com/liquid-analysis-sample-cups/sample-cups

The bottom of the sample cup is covered with an X-ray transparent film. The chemical resistance depends on the material and the thickness of the film:

Film	Thickness / µm	Suitable for	Unsuitable for
Mylar	1,5	Gasoline, Diesel, Solvents	Acids, Bases
Mylar	2,5	Gasoline, Diesel, Solvents	Acids, Bases
Mylar	3,5	Gasoline, Diesel, Solvents	Acids, Bases
Mylar	6	Gasoline, Diesel, Solvents	Acids, Bases
PETREOX	3	Gasoline, Diesel, Solvents	Acids, Bases
Polypropylen	4	Diluted Acids	Gasoline, Diesel, Solvents
Polypropylen	6	Diluted Acids	Gasoline, Diesel, Solvents
Polypropylen	12	Diluted Acids	Gasoline, Diesel, Solvents
Polycarbonat	5	Gasoline, Diesel	
Kapton	7,5	Aromates	

This table gives an overview of the commercially available films. In principle, two materials are used: polyester (Mylar and PETREOX) and polypropylene. The film materials differ in their resistance to chemicals. While polyester is stable against solvents, aliphates and fuels, polypropylene shows more stability against oxygen-rich liquids (e.g. water, polyglycols, high-boiling oils).

A list of available slides can be found here:

https://www.fluxana.com/liquid-analysis-film/thin-films

Choosing the right analytical film is crucial for reliable XRF results. Depending on the sample type, Mylar or polypropylene offer suitable alternatives to PETREOX and Etnom®, whereby a film change should always be evaluated on an application basis and followed by a recalibration.

Transparency for the fluorescence radiation of the light elements from sodium to sulfur is the deciding factor for use of a film. The thinnest Mylar film with 1.5 µm absorbs 50% of the sodium radiation; 6 µm Mylar almost 100%. Analysis of the even lighter element, fluorine, in samples measured with a film is thus impossible. This image provides an overview:

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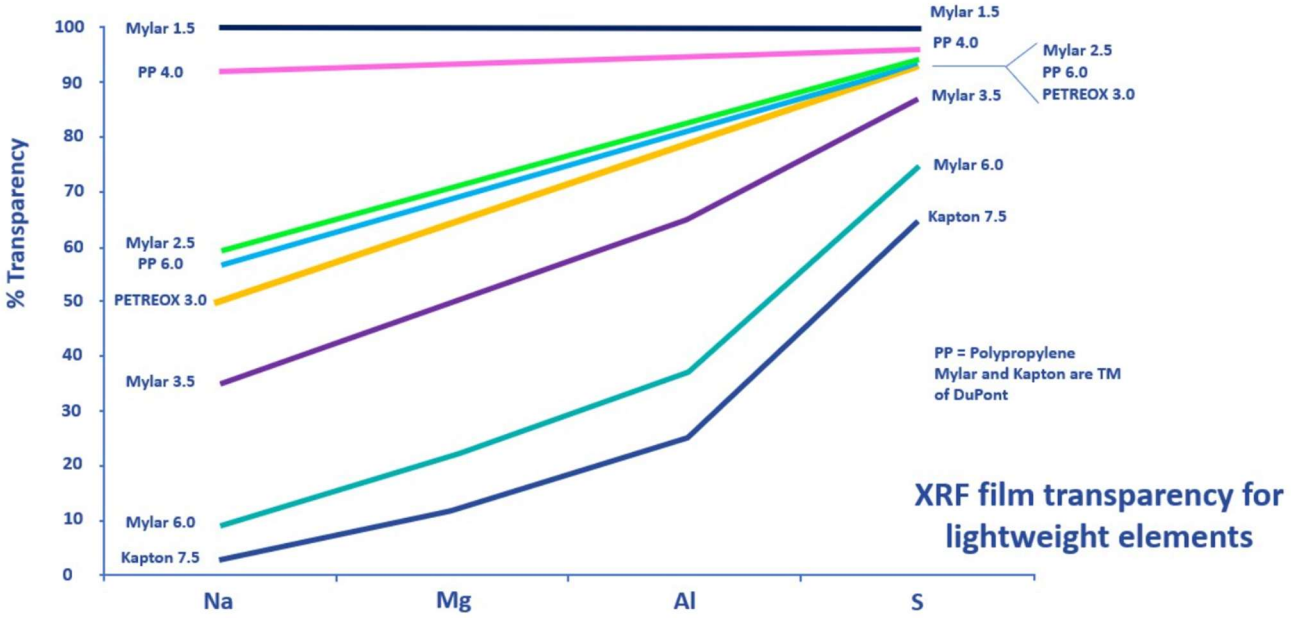

Polypropylene is especially suited to the trace analysis of solid samples, as it has no major contamination in it. In contrast, **Mylar** contains the undesirable phosphorus and calcium (3.5 µm Mylar corresponds to 50 ppm Ca and 250 ppm P in a blank oil, e.g., clean white oil). **PETREOX** contains also phosphorus and Silicium (3.0 µm PETREOX corresponds to 20 ppm P and 600 ppm Si, also in blank oil).

Films such as **Hostaphan** (polyester with a silicon contamination) or polycarbonate (without contamination, preferred for fuel analysis) are restricted or no longer available.

Kapton is not very transparent for the fluorescence radiation of light elements and is, therefore, only useful for the analysis of elements with a higher atomic number.

Correct preparation of the sample cup

With sample cups, the analytical error depends on the preparation of the sample cups. The exact fit of the film, the outer ring and a defined height are decisive. The distance of the X-ray tube from the film on the cup must always be constant. For this reason, it is important to be sure that the outer ring of the cup, which holds the film, must be pulled up enough so that the film touches the bottom of the holder or is at the same height.

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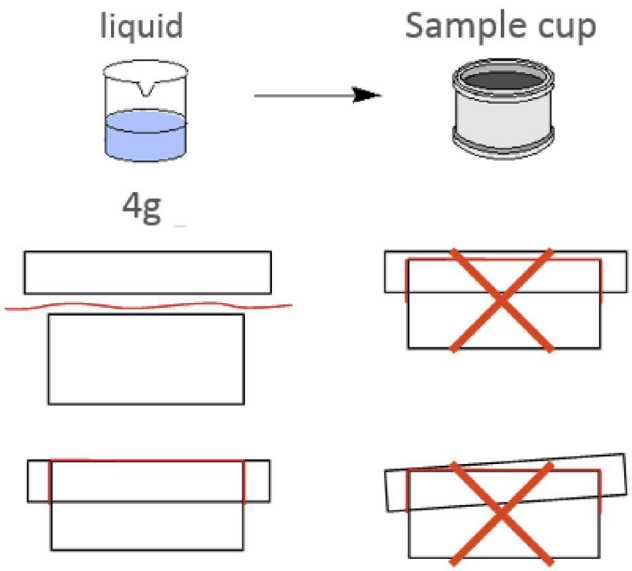


If available, it is advisable to use a lid, as this makes handling easier and minimizes the risk of spillage. In addition, some liquid samples evaporate during the measurement, and a lid can prevent liquid from entering the measuring device.

If you don't want to insert your cuvette yourself and want to save yourself time, there is an alternative option to order ready-made cuvettes.

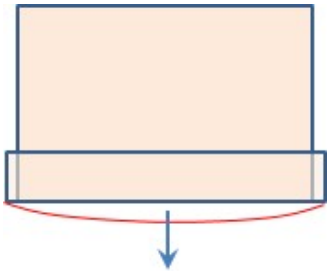
Further information can be found here:

https://www.fluxana.com/liquid-analysis-prepared-cups/prepared-sample-cups

High power WDXRF X-ray radiation shows interaction with the film:

- Polypropylene sags easily
- Polyester shows no change

The radiation contamination of the film, which leads to sagging, can be greatly reduced by using a thin primary filter (e.g. Al).



EDXRF and WDRFA instruments with low power (<50 watts) do not show this effect.

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How much sample needs to go into the sample cups?

Depending on the XRF instrument used, different geometries arise that determine the analyzed volume and the penetration depth. In addition, the quantity depends on the diameter of the sample cup. It is important that the filling height remains constant and that sufficient sample quantity is ensured.

Special cases for liquid samples

Liquids containing particles and liquids with multiple phases, e.g. liquid waste samples (recycling sector):

In this case, absorption by a binding agent (CELLEOX®) mixed with the sample is recommended. This results in a solid paste that is put into the sample cup with a stamp and then measured.

Solid fat samples (lubricating greases):

Here, the use of so-called BOREOX® cups (small pressed pellets with a recess) is recommended, into which a defined amount of the fat is applied, e.g., with a spatula. The BOREOX® cup is then placed into a sample cup and can be measured.

Conclusion: For reliable XRF results and safe operation of the analyzer, the right selection of sample cup and film, as well as careful sample preparation are crucial. In addition to the chemical resistance and the intrinsic content of the film to relevant elements (impurities), geometric influences should also be taken into account: A correctly and flat stretched film and a precisely assembled sample cup with a defined height avoid measurement errors. If the recommended measurement conditions are also observed, leaks, equipment contamination and analytical errors can be reliably avoided.

Summary

To successfully measure liquids, the correct

- sample cup
- film
- procedure

must be selected.

Literature

[1] Rainer Schramm, X-Ray Fluorescence Analysis: Practical and Easy, 2nd edition, FLUXANA (2017).

[2] www.fluxana.de