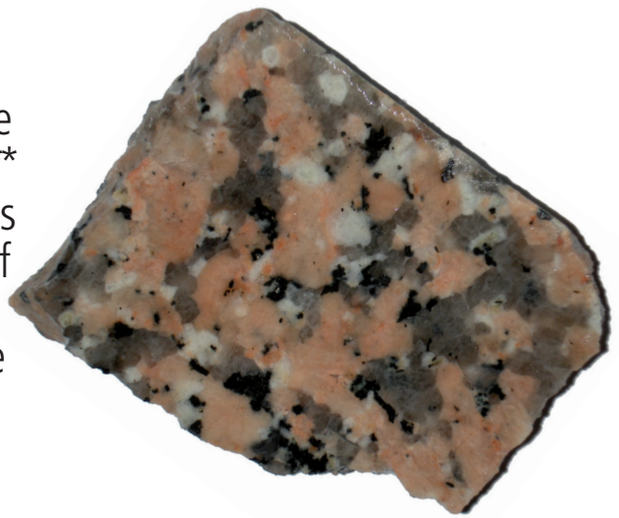
Small spot analysis in glass production

Small spot analysis on glass is important to widen the usual capabilities of X-ray fluorescence analysis. Didier Bonvin* and Christopher Shaffer** explain how narrowing a sample surface analysis area down to 0.5mm and obtaining chemistry of an inclusion or irregularity has helped scientists solve problems once only possible through more complex techniques.



▲ Fig 1. Example of an inhomogeneous sample.

It is well known that the wavelength dispersive X-ray fluorescence (WDXRF) technique is one of the most versatile analytical methods for elemental analysis of solids, including glass. The technique and analytical methods are mature enough to establish clear qualitative and quantitative characterisation of diversified materials. Modern technological developments have helped to include WDXRF into standard test methods for analytical laboratories by virtue of its simplicity and reliability.

Now, process control, failure troubleshooting and in-situ identification are possible using a standard laboratory WDXRF with the advent of small spot/mapping capability. The ability for small spot analysis on glass is important to widen the usual capabilities of X-ray fluorescence analysis. Narrowing a sample surface analysis area down to 0.5mm and obtaining chemistry of an inclusion or irregularity has helped scientists solve problems once only possible through more complex techniques.

Thermo Scientific's Arl Perform'x 4200 WDXRF spectrometer means analyses can be either qualified or quantified by measuring either the whole surface of a sample or a chosen spot on the sample surface.

Small spot analysis

Small spot analysis is a selection of one or more individual points on a sample surface, each one producing a singular analysis result. Mapping is the joining of these individual points into a unified pattern to produce a 2- or 3D presentation along with intensity/concentration results for the selected area.

The first step in small spot analysis is for the XRF unit to image the sample surface. From this image it is possible, using the mouse, to click on areas of interest to designate analysis areas.

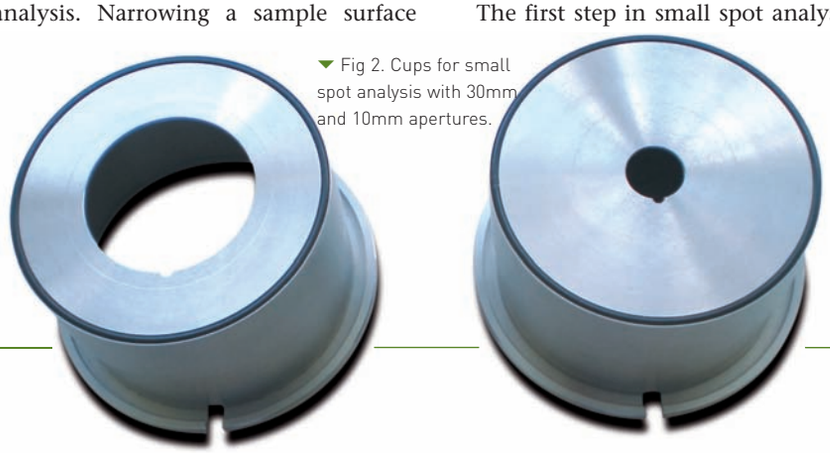
For mapping, the operator would select one of a number of 'shapes' and enlarge it to a size which best contains the area of interest.

The small spot analysis size allows determination of embedded particles or inhomogeneous specimens (***Fig 1***) and product failure investigations. Given a choice of 1.5mm or 0.5mm analysis size, the spectrometer can offer a complement to bridge the gap between traditional WDXRF bulk analysis with a typical analysed diameter of 29mm and standard micro-analysis using microscopic techniques such as SEM (***Fig 2)***.

Standard-less analysis

A development in the analytical programmes in XRF has been the availability of 'standard-less' packages. These packages allow for quantitative data to be obtained for completely unknown samples.

Obtaining enough standards to create a calibration is not always possible. This



▼ Fig 2. Cups for small spot analysis with 30mm and 10mm apertures.

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is certainly the case when analysing defects or unknown contaminations. In such situations, it is best to employ a standard-less software on the market such as the Thermo Scientific UniQuant package.

UniQuant uses a factory calibration based on 64 pure element standards that allows for concentration determination of unknown samples in any matrix by using complex mathematical algorithms for up to 79 elements. These algorithms correct for matrix effects as well as inter-elemental effects to provide precise quantitative results.

Peak hopping, instead of using a continuous scan technique such as other semi-quantitative software programmes, allows for faster analysis by not wasting measurement time on any location where an element peak will not be found or the time to climb and descend existing peak shoulders.

The peak hopping method measures every theoretical 2-theta angle for each element, including alternative lines for heavier elements and background positions. By focusing the elemental counting times to only peak locations, UniqQuant can provide more accurate results and lower detection limits. compared to other scan based semi-quantitative methods.

Inclusion in glass

Combining both small spot analysis and a standardless routine software package provides a powerful tool to solve application problems.

As an example of the technique, glass samples have been submitted for analysis. One of the samples shows a shiny inclusion that we could not determine in the traditional way (***Fig 3***). This sample was analysed with UniQuant to obtain the global composition over a diameter of 29mm. Pre-defined UniQuant counting times, analytical conditions and parameters with regard to crystal, detector, collimator and power were used.

As the sample is a glass the results are expressed as oxides (***Table 1***). Such global analysis does not permit to assess if the shiny inclusion affects the elemental determinations.

Small spot analysis was performed on the shiny inclusion to determine the nature of the inclusion (***Table 2***). This analysis quickly provided the information that the shiny particle was made principally of copper.

Element Si also appears in the spot analysis because the particle is smaller than 0.5mm in diameter and therefore the area of analysis partly includes the glass matrix.

Mapping imaging is a helpful way of understanding a problem. The 2D images can be viewed as individual element distributions or overlaid to give a comprehensive correlation of the elements as a group.

The 3D images are single element display and can be rotated for full 360-degree visualisation or even a birds-eye view. Geological samples can offer the most interesting and informative mapping images.

In this example, one can see the base material being Mn due to its uniform base and strong intensity response but also other elements present with a large formation of Si to one side and the presence of possibly a Ca, S, P vein running through the centre of the sampled area.

While most maps are collected as intensity only images, empirical calibrations can also be used to quantify the results.

Oxide/Element	Conc %	StdErr %
SiO_2	69.77	0.23
Na_2O	12.16	0.16
CaO	7.57	0.13
MgO	3.54	0.09
Al_2O_3	1.09	0.05
K_2O	0.330	0.016
SO_3	0.215	0.011
Fe_2O_3	0.200	0.010
TiO_2	0.0704	0.0035
BaO	0.0239	0.0052
Cl	0.0228	0.0011
CuO	0.0175	0.0009
MnO	0.0118	0.0007
ZrO_2	0.0091	0.0005
P	0.0073	0.0006
Cr_2O3	0.0069	0.0006
SrO	0.0066	0.0003
SnO_2	0.0018	0.0009
ZnO	0.0016	0.0004

StdErr = Estimated uncertainty

▲ Table 1. UniQuant elemental determination of the glass sample.

Element	Shiny particle	Glass surface
Al	0.74	0.50
Cu	24.34	0.02
Fe	1.57	0.16
Sn	1.19	0.50
Si	34.84	70.46

▲ Table 2. Spot analyses (all values in %).

Conclusion

Investigative abilities using WDXRF have been shown to save thousands of dollars in process monitoring.

Small samples are no longer a hindrance due to size and lack of calibrating materials, when using complex mathematical algorithms.

Coating thickness across a surface is now possible to review without the need of specialised instrumentation.

Quantification using empirical calibrations on undersized or irregular shaped materials is possible through the use of a standard laboratory WDXRF, even in-situ. ■

***Didier Bonvin, X-ray Product Manager, Switzerland, Thermo Fisher Scientific**
****Christopher Shaffer, Arl Perform'x Product Manager, Switzerland, Thermo Fisher Scientific**
Website: www.thermofisher.com

◀ Fig 3. Glass sample with shiny inclusion.