

improvement of the X.R.F. results as compared with the target compositions. The X.R.F. analyses compare favourably with the chemical analyses but the poor correlation with the target values shows that other sources of error are present in addition to matrix effects.

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Experiences with electron beam analysis with particular regard to sodium and fluorine

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Electron excitation appears to offer higher rates of analysis of glass and raw materials than using sealed X-ray tubes alone. There are however, certain disadvantages. These lie mainly in the areas of sample preparation which is the limiting factor in the present sample reproducibility, and arise principally from the need to make the samples conducting.

Further work on alternative systems such as conducting surface coatings and grids would be welcome and may

eliminate some of these problems by permitting the use of fusion techniques which would probably give greater reproducibility of sample preparation. Although there is plenty of intensity for the light elements even higher count rates obtainable by using thinner counter windows and better reflecting crystals such as RbAP, should permit the reduction of beam current and so reduce the peculiar effect of loss of sodium intensity on repeat determinations.

Expériences d'excitation par un faisceau d'électrons portant plus spécialement sur le sodium et le fluor

Il semble bien que l'excitation par un faisceau d'électrons permette d'analyser les verres et les matières premières plus rapidement que les tubes à rayons X scellés. La méthode présente toutefois certains inconvénients au niveau de la préparation des échantillons, dont la reproductibilité est actuellement limitée par le fait qu'ils doivent être rendus conducteurs.

Des travaux plus poussés sur d'autres systèmes, tels que revêtements et réseaux superficiels conducteurs, seraient nécessaires pour résoudre certains de ces problèmes. Ils

permettraient d'utiliser des techniques de fusion qui conférerait sans doute une meilleure reproductibilité à la préparation des échantillons. Bien que l'intensité soit suffisante pour les éléments légers, les vitesses de comptage plus élevées que l'on pourrait obtenir en utilisant des fenêtres de compteurs plus minces et des cristaux plus réfléchissants (tels le RbAP) devraient permettre une réduction d'intensité du faisceau et donc une diminution de l'effet particulier de la perte d'intensité du sodium en cas de dosages répétés.

Erfahrungen bei der Elektronenstrahlanalyse insbesondere in bezug auf Natrium und Fluor

Die Methode der Elektronenanregung scheint eine schnellere Analyse der Gläser und Glasrohstoffe zu ermöglichen als die ausschließliche Anwendung von Röntgenröhren. Gewisse Nachteile können hier aber nicht übersehen werden. Sie liegen in der Hauptsache auf dem Gebiet der Probenpräparation, die die Reproduzierbarkeit der Probe einschränkt, und sie entstehen prinzipiell aus der Notwendigkeit, die Proben leitfähig zu machen.

Eine weitere Untersuchung der Möglichkeiten, die die Probenoberfläche durch Beschichtung oder ein Gitter leitfähig machen, ist notwendig. Dabei würden einige Probleme

beseitigt, da das Schmelzverfahren angewandt werden könnte und damit wahrscheinlich eine bessere Reproduzierbarkeit der Probenpräparation gegeben wäre. Obwohl schon hohe Intensitäten für die leichten Elemente gemessen werden, sollte gerade eine Erhöhung der Zählraten, die durch die Anwendung dünnerer Zählrohrfenster und besser reflektierender Kristalle — z. B. RbAP — erzielt werden kann, die Erniedrigung des Probenstroms gestatten und damit bei Wiederholungsbestimmungen den besonderen Effekt der Intensitätsverminderung bei der Natriumanalyse reduzieren.

The decision to set up a central analytical control laboratory at Rockware Glass almost inevitably meant the introduction of an instrumental technique to handle the resulting work load. The advances made in the technique of X-ray fluorescence towards the more

efficient analysis of the lighter atomic number elements made it probable that this would be the method used. There was however, some doubt about its ability to analyse sodium and less importantly fluorine, with the precision required to control these elements in the

finished glass. Ideally, it was wished that the technique chosen be able to analyse with the required precision, all the major elements of interest, sodium being one of these, and so the ability of the X-ray fluorescence to cope with this particular element was of prime importance. This was particularly so in the present case as the proposed laboratory was entirely new and it was not wished to have to build up experience and technique in other directions to fill any gaps left by an instrumental technique, be it X-ray fluorescence or any other.

1. Instrument evaluation

The results of analyses carried out by various instrument manufacturers indicated that using a 1,7 kW chromium target tube and a 2 μm polypropylene counter window intensities of the order 10 counts per second per one percent sodium oxide (10 cps/1% Na₂O) and about 0,5 counts per second per one percent fluorine could be obtained. More than adequate intensities were available on all the other elements of interest, the only difficulty being possibly in the determination of low levels of chromium. Whilst the count rate for sodium was reasonable, it was still felt that count times for a complete analysis could be rather long.

Looking for an increase in performance in sodium analysis and the possibility of carrying out fluorine determinations also, it was then decided to examine an instrument using both electron beam and X-ray excitation. Tests with this instrument using electron excitation for the elements silicon downwards showed increasing intensities over the chromium tube as the atomic number decreased rising to a factor of ten at sodium. This initial work was done with low beam currents (about 150 microamps sample current) using a 6 μm mylar window. This thickness of window completely absorbed all the fluorine radiation emitted. Further tests with a thinner (3,5 μm) window and higher beam currents showed increased count rates of about 250 cps/1% Na₂O and 20 cps/1% F. These intensities appeared to offer considerably reduced analysis times, and hence a greater throughput of samples, over the best chromium tube instrument. Tables 1 and 2 show this in a much clearer way with manufacturers predicted programme times using the two alternative systems on the two materials of greatest interest. The advantage in time of the electron beam is clear. The very much higher intensities obtained particularly on sodium, should lead to quicker analytical times and greater sample throughput, and for this reason the decision was made to purchase the electron beam instrument.

2. Electron beam and X-ray excitation compared

The main advantage of using direct electron excitation as against a sealed X-ray tube is the greater excitation efficiencies obtainable for the lighter elements i.e. silicon downwards. Secondly in combination with a medium or heavy element target X-ray tube optimum excitation can be obtained for a wide range of elements.

Electrons because of their lower energies do not penetrate so deeply into the sample as X-rays and hence interelement effects are also reduced. The main disadvantages of electron excitation are:

- a) the sample must be conducting,
- b) the beam stability is not as good as a sealed X-ray tube,
- c) the samples deteriorate more rapidly under electron bombardment than under X-ray bombardment.

Table 1. Glass analysis

oxide	Cr tube, 2 μm window	EB/W tube, 3,5 μm window	
	count time in s	count time in s	
Na ₂ O	200	18	EB
K ₂ O	10	30	XR
CaO	10	30	XR
MgO	100	18	EB
Al ₂ O ₃	40	18	EB
Fe ₂ O ₃	4	10	XR
Cr ₂ O ₃	4	10	XR
SO ₃	40	18 + 18	EB
goniometer winding print out etc.	90	90	
total time	498 s	260 s	
Cr tube	1,7 kW		
W tube	1,8 kW		
EB	10 kV/300 microamps sample current		

Table 2. Sand analysis

oxide	Cr tube	EB/W tube
	count time in s	count time in s
Na ₂ O	200 + 200	18 + 18
K ₂ O	10	30
CaO	8	10
MgO	10 + 10	18 + 18
Al ₂ O ₃	40	18 + 18
Fe ₂ O ₃	4	10
Cr ₂ O ₃	10 + 10	10 + 10
TiO ₂	4	10
winding time print out etc.	90	90
total time	596 s	276 s

How do these advantages and disadvantages compare against the present particular requirements?

1. We are interested in the lighter atomic number elements, silicon, aluminium, magnesium, sodium and fluorine.

2. The sample must be conducting. Certainly glass and its raw materials are not conducting, so the sample preparation technique adopted will have to make them so. There could thus be a problem here.

3. The stability of the electron beam is not as good as the sealed X-ray tube, but by using the sample current to control the analytical time required precisions can be obtained. Count rates obtained using electron excitation are so much higher that the accumulation of more counts to give greater statistical precision can easily be done, in a shorter time than with an X-ray tube. There should not be a serious problem here.

4. Sample deterioration. If in fact the samples do deteriorate more rapidly under electron bombardment, this could be very inconvenient, leading to shorter lives on standard pellets and the necessity to replenish these more frequently.

Summarising therefore, in glass and raw material analysis we are interested in the lighter atomic number elements, which are excited much more efficiently by the electron beam than by an X-ray tube.

Elements potassium to chromium which are also of great interest can be efficiently excited even by heavy element target tubes such as tungsten. The electron

Table 3. Count rates for lighter elements in glass using 10 kV electrons and 300 microamps sample current

aluminium	1550 cps/1 % Al ₂ O ₃
magnesium	1350 cps/1 % MgO
sodium	880 cps/1 % Na ₂ O
fluorine	85 cps/1 % fluorine

Table 4. Sand analysis, precisions

oxide	concentration in %	coefficient of variation in %	2 σ in \pm %
Na ₂ O	0,70	3,7	0,05
K ₂ O	0,65	0,06	0,008
CaO	0,45	3,2	0,02
MgO	0,30	2,8	0,02
Al ₂ O ₃	3,00	1,1	0,07
Fe ₂ O ₃	1,80	1,2	0,04
TiO ₂	0,30	4,8	0,03

Table 5. Glass analysis, precisions

oxide	concentration in %	coefficient of variation in %	2 σ in \pm %
Na ₂ O	15,00	0,7	0,20
K ₂ O	0,50	0,2	0,002
CaO	9,30	0,4	0,08
MgO	0,40	2,2	0,02
Al ₂ O ₃	2,40	0,8	0,04
Fe ₂ O ₃	1,20	0,4	0,01
Cr ₂ O ₃	0,20	0,2	0,008

beam although inherently less stable than a sealed X-ray tube, can be monitored to give precisions of an acceptable level. The sample does deteriorate under electron bombardment but this is not a serious problem. The production of conducting samples of glass and its raw materials can lead to greater sample preparation problems than with conventional X-ray excitation, but these problems can be overcome, as shown in the next section.

3. Sample preparation

The method of sample preparation originally envisaged was to grind the sample to a fine powder using a disc mill, to mix the sample with graphite and possibly binder (both in fine powder form) and to press the mixture in a die to produce a strong disc for examination. It was felt that a suitable sample of glass would only be obtained by grinding to a fine powder because of the difficulties of obtaining a flat portion from most containers. Sample preparation has in fact given rise to several problems. These were briefly:

- the difficulty in obtaining fine enough powders to give the required reproducibilities;
- comparatively long grinding and mixing times to do this (ten minutes grinding and ten minutes mixing),
- finding a suitable mixing process without burning the binder,
- burning of the sample by electrons,
- surface effects causing variations in measured intensities.

All these problems were confined to the elements sodium and fluorine only. No real difficulties were experienced in obtaining adequate reproducibilities for

the other elements. By using the disc mill as a mixer as well as a grinder and carrying out a study of various grinding and mixing times it was possible to evolve a standardised technique. The effect of the binder burning off was eliminated by mixing the binder separately after the glass and graphite mixing. Finally, by experimenting with glass to graphite ratios it was possible to eliminate the use of a binder altogether, albeit with some sacrifice in the mechanical strength of the pellets.

At first this gave problems due to insulation breakdown from graphite shorting to earth, but this was simply overcome by coating the sample insert with a resin.

Methyl cellulose binder is still used in sands, feldspar and refractory samples. Sometimes the surface is bloomed if the binder is not perfectly dry. This leads to high results and has to be eliminated by crushing and recompacting the pellets to obtain a shiny surface.

4. Electron beam stability and count rates

The beam stability was not expected to be worse than three times that theoretically calculated from the number of counts obtained. In practice it was found this figure varied between two and two point five. By fitting permanent magnets to the collimating slits this factor has now been reduced to 1,5. The figure of 1,5 includes angular resetting errors and instrumental drift over an eight hour period. The magnets also reduced the background level leading to improved peak to background ratios and hence even lower limits of detection. Count rates have been further increased by redesigning the window mounting grid and using 2 μ m windows. Using 10 kV electrons and 300 microamps sample current, fine (254 μ m apertures) collimation and a KAP crystal count rates for the lighter elements in glass are now as follows in Table 3.

5. Sample deterioration

There is one peculiar disadvantage of the electron beam system when analysing glass and that is the falling off of the sodium intensity on repeated measurements. The rate of fall in intensity depends on the length of time of irradiation and the beam current. This effect is well known in electron probe work where it is much more marked due to the higher power input per unit surface area. It is minimised by reducing the beam power and increasing the irradiated area.

In practice using the beam currents and count times necessary to obtain accurate results, it was found that each sample face can be irradiated twice before the drop in intensity is significant i.e. by using both faces each standard sample can be used four times.

The present procedure therefore is to make a set of secondary sodium standards and by scheduling the samples so that the maximum number can be run off in one day, using the calibration curve to the full.

With regard to other effects of the beam, we have not experienced any difficulties. In fact on one occasion one sample has been run for sixteen hours continuously through a complete programme of five electron beam and five X-ray channels. The sort of results we are achieving in practice in routine control operation are shown in the Tables 4 and 5. Finally, it has been possible to analyse for F at the 5% level in opal glasses with standard deviations of 0,10% F at a count time of 18 s.