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A borax fusion technique for quantitative X-ray fluorescence analysis

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THE BORAX FUSION technique is a well known sample preparation method in quantitative X-ray analysis. The advantages of the method are that standards can be easily prepared and that no particle-size problem arises. Several variations of the method have been published.[1-9] The need for these has arisen because of lack of reproducibility.

We report a variation of the borax fusion technique which is reproducible and does not require a skilled operator. The method is based on the observation of Zuurbier and Thomson[10] that molten borax poured on "Degussa Geräteplatin II" (a 95:5 Pt/Au alloy) will loosen after its solidification and yield an intact glass disc with a specular surface.

EXPERIMENTAL

Platinum casting moulds

These were formed from polished sheet "Degussa Pt II" (50 mm diameter × 0.2 mm thick). A die of the form shown in Fig. 1 is clamped in a lathe and a circular platinum sheet is concentrically

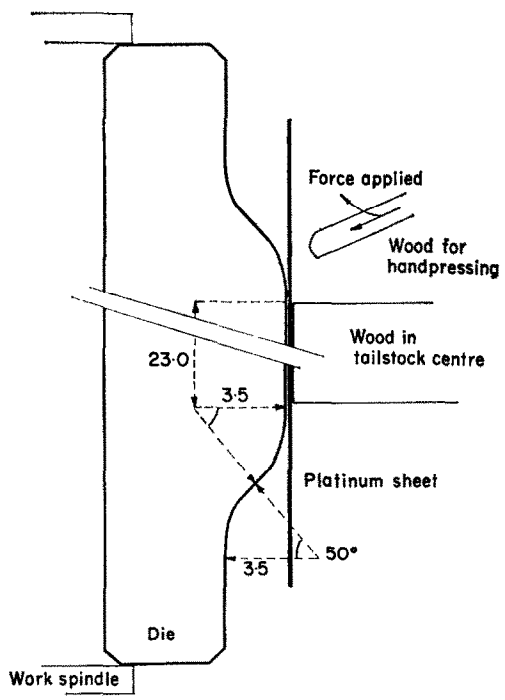

FIG. 1.—Form of the die and arrangement for the forming process.

held against the die by a piece of wood in the tailstock centre. While the lathe is spinning the platinum is manually pressed against the die by means of another piece of wood. After forming, the platinum sheet is removed from the lathe and heated to reduce strain. The process is repeated four times until the fit of mould to die is satisfactory. Then the inner surface of the mould is slightly sand-blasted and next polished with cotton and some household silver polish. Instead of sand-blasting a satisfactory procedure is to press the mould between the die and a counter die of such form as to leave exactly the space for the thickness of the platinum.

The dimensions of the die are not critical, but it has appeared essential for loosening of the glass discs that the radius should not be appreciably below 3.5 mm and the angle above 50°.

The flux

This was prepared in batches of about 1½ kg by mixing in a cube mixer for 3 hr the following chemicals: 45 parts by weight anhydrous sodium tetraborate, 7 parts by weight lithium hydroxide powdered to approximately 80-mesh, 16 parts by weight of orthoboric acid; when kept over silica gel in a desiccator the flux is stable for at least 6 months. The quantitative composition is not very critical, but for standards and samples the same composition should be used.

Heavy absorbers

Lead(II) oxide.
Tungsten(VI) oxide.
Barium sulphate.
Lanthanum oxide.
Cadmium oxide.

Procedure (molybdenum in alumina catalyst)

Accurately weigh 100 ± 5 mg of powdered sample (Note 1), add 1200 ± 1 mg of barium sulphate (Note 2) and an amount of flux up to 8000 ± 1 mg (Notes 3 and 4).

Mix the powders in a platinum crucible by stirring with a spatula and heat over a Méker burner at 1200° until molten. Protect flame and crucible with a firebrick heat-shield. Keep the sample mixture molten for another 2–5 min with occasional swirling to promote homogeneity. Take care that all gas bubbles are removed. Meanwhile heat a casting-mould until nearly red hot; the temperature of the mould is not critical.

Pour the contents of the crucible into the mould and allow to cool. The glass disc will loosen from the mould during cooling. Remove the glass disc from the mould. Sand-paper the rim of the glass disc, if necessary, so that it fits in a sample holder for the fluorescence measurement. Use a sample holder with a mask of <23 mm diameter.

Prepare standards from the appropriate oxides or salts of the element to be determined. They are stable for at least one year, if kept in a desiccator with silica gel.

Notes

1. Metallic samples should be previously converted into oxides or salts.
2. Instead of barium sulphate, other heavy absorbers may be used. Those mentioned above are satisfactory.
3. The relative amounts of the sample, the heavy absorber and the flux may be changed, although fracturing of the glass discs may occur when the amount of absorber and sample is increased.
4. If the sample contains a large amount of copper the addition of 200–500 mg of sodium or potassium chloride prevents fracturing of the glass discs. This addition also guards against fracturing in the case of certain combinations of elements (*e.g.*, Ti and Zr with PbO as heavy absorber).

RESULTS AND DISCUSSION

With homogeneous samples the relative standard deviation[11] can be as low as 0.2%. These deviations include the deviations due to sampling and weighing and those due to instrumental short-time drift and unequal sample positions (0.1%).

Most elements give good clear discs when present in amounts of 100 mg. Some may be present in such amounts that they can be used as the heavy absorber. The following elements give intact glass discs, but the glass is not clear and may not be homogeneous: Zn, Nb, Ru, Rh, Pd, Sn, Te, I, Ir. The following elements either do not give intact discs or cause other difficulties: As, Ag, Au. It should be noted that the compound used may be of importance, *e.g.*, chromium(III) oxide gave a "cloudy" disc, chromium(VI) oxide a clear one.

In this method the samples are diluted substantially. A loss in sensitivity has therefore to be accepted. The method is, however, advantageous for an accurate determination of major constituents.

The method is also relatively rapid. Two hours is ample time for a duplicate determination if the standards have already been prepared. When several elements can be determined in one glass disc and/or when the sample is brought into solution with difficulty this time compares favourably with the time needed for wet methods.

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Summary—A borax fusion technique to cast glass discs for quantitative X-ray analysis is described in detail. The method is based on the "non-wetting" properties of a Pt/Au alloy towards molten borax, on the favourable composition of the flux and finally on the favourable form of the casting mould. The critical points of the technique are stressed, resulting in a method which could be carried out successfully by inexperienced workers. In general the method compares favourably in speed and accuracy with wet-chemical methods.

Zusammenfassung—Ein Schmelzverfahren mit Borax wird im Detail beschrieben, um Glasscheiben für die quantitative Röntgenanalyse zu gießen. Das Verfahren beruht darauf, daß eine Pt/Au-Legierung von geschmolzenem Borax nicht benetzt wird, ferner auf einer günstigen Zusammensetzung des Schmelzflusses und auf der günstigen Gestaltung der Gußform. Es wird Nachdruck auf die kritischen Punkte des Verfahrens gelegt; daher sollte es auch von Unerfahrenen mit Erfolg ausgeführt werden können. Im allgemeinen schneidet das Verfahren bezüglich Geschwindigkeit und Genauigkeit im Vergleich mit naßchemischen Methoden günstig ab.

Résumé—On décrit en détail une technique de fusion au borax pour couler des disques de verre pour l'analyse aux rayons X quantitative. La méthode est basée sur les propriétés "non-mouillantes" d'un alliage Pt/Au vis-à-vis du borax fondu, sur la composition favorable du fondant et finalement sur la forme favorable du moule de coulée. On fait ressortir les points critiques de la technique, avec pour résultat une méthode qui pourrait être exécutée avec succès par des travailleurs inexpérimentés. En général, la méthode est favorablement comparable en rapidité et précision avec les méthodes chimiques par voie humide.

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