Preparation of glass standards for the use in X-ray microanalysis

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SUMMARY. Homogeneous glasses for the use as standards in electron-probe microanalysis were prepared as an alternative to natural minerals, oxides, and pure minerals. Homogeneity was achieved by careful grinding, mixing, and fusion of powders of known composition. Fusion was carried out under vacuum using a molybdenum boat. This method avoided bubbles and contamination and made it possible to achieve temperatures high enough for final mixing to occur during the fusion process. Nine glass beads each containing six to seven oxides were subjected to careful micro-probe examination. A statistical analysis of the results showed that for each element there was no significant difference in composition between the spots measured. As the analysing spot was of diameter $0.8\,\mu$, this showed that the glasses were homogenous on a sub-micron scale.

IT is well known that the accuracy of X-ray microanalysis depends largely on the possession of a set of suitable standards. Ideally, these should satisfy the conditions discussed by Sweatman and Long (1969, p. 341), with respect to such factors as homogeneity and stability under electron bombardment. An additional point is that the composition of the standard should be as close as possible to the unknown in order to minimize correction factors, the calculation of which still involves some uncertainty.

The standards most widely used are pure minerals, oxides, and metals so that some correction of the intensity ratios is necessary unless the composition of the standard approximates closely to that of the unknown. The use of oxides and metals always involves a considerable correction factor when silicates are analysed.

Glass standards seem to present a way of avoiding most of these difficulties, particularly those in which glasses of the same composition as the unknown mineral can be prepared. With the exception of alkali glasses, which are unstable under electron bombardment (Vassamillet and Caldwell, 1969), synthetic glasses satisfy the conditions necessary for electron-probe microanalysis. Differences between bonding or valency in the standard and unknown should not give rise to significant errors of intensity ratios because the atoms of a glass are linked by forces similar to those of crystals to form extended, three-dimensional networks, which do not possess the symmetry of crystalline networks but are not completely random. Thus for an oxide to exist in a vitreous state, it must form a network of energy approximately the same as its crystalline modifications. This demands that the oxygen polyhedra surrounding the cation shall be the same in the glassy and crystalline form (Zachariasen, 1932).

Each of the glass standards prepared is composed of mixtures of seven oxides corresponding in composition to a wide range of minerals, e.g. most garnets, pyroxenes, and amphiboles can be successfully fused. In other cases, such as staurolite, where

it is practically impossible to prepare a glass with the appropriate composition, mainly due to the high alumina content, it is necessary to prepare a glass or range of glasses with the same mass absorption coefficients, etc. for the elements present as those possessed by the unknown. This obviously does not overcome the correction un- certainty, but does, at least, offer the advantage of accurately known chemical composition and availability. Further, the method avoids the necessity for making the lengthy calculations involved in the correction procedure.

In most cases, the main objection to the use of glasses appears to be the difficulty found in achieving the required homogeneity on a sub-micron scale (Sweatman and Long, 1969, p. 341). The present paper describes attempts by the author to produce this degree of homogeneity.

Theoretical considerations. In order to form a glass of any kind there must be sufficient glass-forming or network-forming ions such as silicon and boron. In many silicates, SiO_2 forms the basic tetrahedral network within which the network-modifying ions such as Na, K, and Ca occupy interstitial positions. In addition intermediate ions, which can partly replace Si, and ions such as Fe^{3+}, Mg^{2+}, or Ni^{2+}, which are partly glass-formers, partly modifiers, may also be present.

The formation of a silicate glass is favoured by its relatively high viscosity, which prevents devitrification. The viscosity depends on the stability of the Si–O bond and the composition of the glass, particularly the presence of Na^+, K^+, and to a lesser extent Ca^{2+}, which tend to distort the tetrahedral symmetry so that a lower viscosity results. Al^{3+} and Ti^{4+} can also produce such an effect if present in too great a quantity.

Experimental

Powder preparation. Spec-pure powders were ground under ether in a pestle and mortar to a mean particle size of 2 to 3 μm. This uniformity of grain-size is very important for ensuring homogeneity of the powder and later the glass. Before weighing, the powders were heated in an oven at 200 °C to ensure total removal of any residual moisture. The weighing was carried out under the driest conditions possible so that the true weights of the oxides were determined. After weighing, the powder is made into a slurry with ether and the container is fitted to a Glen Creston sample mixer mill and left to run for 3 hr. This produces a well-mixed powder with no graded settling of varying particle sizes because of the initial uniformity of grain-size. The ether is evaporated off and the powder is then again ground and mixed in the mortar for a further 1 to 2 hr—the particles at this stage being virtually colloidal.

Fusion. Two methods were available to the author: fusion in a muffle furnace, or adapting an Edwards vacuum-coating unit for fusion under vacuum and in air. The glasses produced by fusion in the muffle furnace at 1400 °C using carbon crucibles showed variation of Fe, Mn, and Ti across the bead in excess of 5 %. Alumina crucibles were considered as an alternative to carbon but these may possibly lead to contamination of the molten glass. It was decided therefore to use the Edwards vacuum unit, which can be adapted to heat various metals between electrodes, achiev- ing temperatures in excess of 1700 °C. A small boat of platinum was prepared and

heated in air in an attempt to fuse the powder. It was found, however, that the platinum was inclined to tear approaching 1000 °C and so fusion was carried out using a molybdenum boat under a high vacuum. This method offers various advantages: no reduction of any of the components occurs since the molybdenum is less likely to react with the glass components at high temperatures; since the initial bead is small (1 to 1·5 mm thick) and the molybdenum boat heats uniformly on all sides except the top, the possibility of a significant temperature-gradient produced by radiation from the top surface is slight; higher temperatures can be achieved, which is important because it ensures that convective currents are set up resulting in greater mixing and hence homogeneity; the molten glass does not wet the surface of the molybdenum, which is contrary to the case with platinum. Instead a small droplet forms resulting in a clear and bubble-free glass bead.

The lens-shaped glass beads measured on the average 8 mm in diameter by 1·5 mm thick. Surface contamination from the molybdenum boat was negligible, they contained few bubbles, and microscopic examination showed that fusion was complete. Only one fusion was necessary, attributable mainly to the initial preparation of the powders.

One disadvantage of the method is that, due to the high temperatures needed for fusion coupled with the high vacuum conditions, oxides of high volatility may be lost. The results indicate that it is inadvisable to use either Na_2O or K_2O. Na_2O was not seriously considered in any case because of its erratic behaviour under electron bombardment (Vassamillet and Caldwell, 1969).

Glasses containing 8 to 10 % K_2O showed an unacceptable level of inhomogeneity. This was overcome by the substitution of CaO as the glass modifier. The other common oxides such as Al_2O_3, Fe_2O_3, SiO_2, etc. are quite stable at the fusion temperatures. In all, nine glasses were prepared and examples of three glasses of varying composition are:

	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MgO	MnO	CaO
I	38·50	0·30	21·00	29·10	2·00	6·75	4·50
II	37·00	0·57	24·99	9·86	4·02	22·48	2·07
III	40·00	2·46	19·02	6·03	12·01	11·25	9·17

These percentages are the amounts of the oxides added. Weighing before and after fusion showed no difference apart from that attributable to loss of CO_2. It is therefore safe to conclude that no significant loss of any oxide occurred. All iron oxide is in the ferric state.
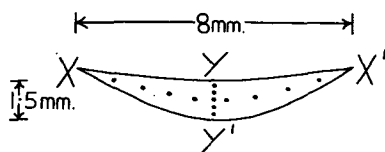
FIG. 1. Spot 0·8 μ.

45–60 μA.
15 K.V.

Examination of the glasses. The glass beads were cut to reveal a central cross-section, polished and coated with a carbon film according to the technique described by Smith (1965, p. 860). Their degree of homogeneity was then examined using the electron probe. All glasses were examined along two main traverses at

right angles—a total of thirteen spots. Because of the fairly severe fusion conditions some compositional irregularities might be expected very close to the glass surface so that marginal spots were taken several microns in from the edge. At each spot five 10 sec counts were taken for each element.

TABLE I. *To show that the ratio of within-spot mean squares to the between-spot mean squares is insignificant at least to the 7 % level*

	Glass I				Glass II				Glass III			
	$\overline{X}$	A	B	100P	$\overline{X}$	A	B	100P	$\overline{X}$	A	B	100P
Si	3420	3182·58	4767·83	15·2	4669	6098·35	10471·42	9·0	4372	3122·40	3481·92	37·0
Al	1245	1347·60	1163·50	55·0	2066	2134·10	1889·08	54·0	1375	856·46	1426·00	10·1
Fe	3052	2288·00	2725·00	30·5	1839	1216·94	1768·08	17·0	1082	786·56	734·65	51·0
Mg	176	95·73	84·33	54·0	571	251·33	223·75	54·0	255	94·17	96·08	44·0
Mn	6356	8482·52	15399·75	7·2	3587	3075·40	5367·42	8·1	1717	1101·92	916·58	57·0
Ca	569	169·73	304·67	7·2	2217	2300·11	1884·75	57·0	1357	637·87	1010·20	12·2
Ti	246	117·02	137·75	32·0	876	834·23	743·75	53·0	1450	911·90	1039·33	34·0

$\overline{X}$—Overall count mean.

A—Within-spot mean square, which estimates σ_w^2, i.e. measure of variation within a random sample of counts on the same spot.

B—Between-spot mean square, which estimates $\sigma_w^2 + 5\sigma_b^2$, where σ_b^2 is a measure of variation between spots. 100P (F > B/A) is the percentage probability of a random variable F, distributed with F (12, 52) distribution exceeding the ratio B/A. In particular, upper 5 % level for F is 1·945.

The results were treated statistically by means of the analysis of variance. The standard deviations between each of the spots were compared and this showed that there were no significant differences (at the 5 % level) in count-rate between any of the spots examined for any of the elements analysed. The entire range of variation measured coincided with the range produced by random variation within a single spot (table I).

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