

PAPERS

The chemical analysis of a fluoride-opal glass described as Standard Glass No. 4

A report of the Chemical Analysis Committee of the Society

In recent years the Chemical Analysis Committee of the Society has conducted investigations into methods of analysis for three different types of glass, and recommended methods for these glasses have been published. The investigation of Standard Glass No. 4 was a continuation of the earlier work which had been directed to the analysis of glasses in common usage. In addition to the constituents determined in the previous series, this glass contained fluorine and zinc.

A quantity of white opal, manufactured in a single plate, was cut into small sections, well mixed, and distributed to the participating laboratories for analysis. After much exploratory work in which the merits of alternative methods were examined, a recommended scheme of analysis was approved.

Nine laboratories then took part in an assessment of the precision of the recommended methods. Analyses were carried out, usually in triplicate and by one analyst in each of the laboratories, and a statistical summary of the results achieved is given.

Samples of Standard Glass No. 4, together with its agreed composition and the recommended methods

of analysis, can be obtained through the Honorary Secretary of the Society.

Percentage composition of the glass

The analytical results obtained on Glass No. 4 by the participating laboratories are given below to indicate the precision obtained with the methods described in the two following Sections. In the original planning of this work it was hoped that a balanced experiment could be carried out so that the variance between and within laboratories could be stated. However, in co-operative work of this nature, which often has to be undertaken as an extra task when time can be found, it is very difficult to adhere to a rigid experimental plan and the present programme was no exception. Thus the standard deviation of all results from all laboratories has been quoted in the table. In any one laboratory a smaller standard deviation might be expected from repeat analyses, and the data available suggest that as a rough guide the standard deviation of repeat analyses in any one laboratory would be about 70% of those quoted. Although this glass contains almost 5%

	Mean value (%)	Standard deviation	Number of results	Number of laboratories
Silica (SiO ₂)	69.49	0.11	17	6
Aluminium oxide (Al ₂ O ₃)	3.02	0.12	24	9
Total iron as ferric oxide (Fe ₂ O ₃)	0.099	0.003	23	8
Titanium oxide (TiO ₂)	0.041	0.002	20	7
Zinc oxide (ZnO)	3.28	0.06	23	9
Calcium oxide (CaO)	4.24	0.05	24	9
Sodium oxide (Na ₂ O)	15.45	0.10	23	8
Potassium oxide (K ₂ O)	0.57	0.04	19	7
Fluorine (F)	4.96	0.10	23	8
Boric oxide (B ₂ O ₃)	0.19	0.02	8	3
Loss on ignition*	0.22	0.09	53	10

Barium oxide (BaO), magnesium oxide (MgO), and total sulphur expressed as sulphur trioxide (SO₃), are each present in amounts of the order of 0.05% or less.

* Study of the variability of the results for loss on ignition showed that the values obtained depended on a variety of factors. Nevertheless, it was thought useful to include those results which were obtained under closely specified conditions.

of fluorine, conventional practice has been followed in expressing all constituents other than fluorine as oxides.

Preparation of the sample, reagents, and apparatus

Preparation of the sample

A sample, sufficient for immediate requirements only, should be finely ground in small portions in an agate mortar. The portions should be well mixed, dried at 110°C for one hour, and allowed to cool in a stoppered weighing bottle stored in a desiccator. The portions for analysis should be weighed immediately after cooling.

Reagents

All the reagents should be free from such amounts of impurities as might endanger the accuracy of the determination in question. Analytical reagent quality will normally be suitable, but provision is made for blank determinations where these are considered to be essential. Distilled or de-ionized water should be used throughout.

Solutions. In the list of reagent solutions given below the following designation is used for the solutions of acids and of ammonia. For concentrated reagent solutions the specific gravity is quoted, e.g. concentrated hydrochloric acid is described as 'hydrochloric acid (sp. gr. 1.18)'. For diluted reagent solutions the proportions by volume in which the concentrated reagent is to be diluted with water is given, e.g. hydrochloric acid (1:4) refers to the solution obtained by diluting 1 volume of hydrochloric acid (sp. gr. 1.18) with 4 volumes of water.

Acetic acid (glacial).

Acetic acid (5:95).

Aluminium chloride solution. Carefully add 5 g of anhydrous aluminium chloride, in small portions at a time, to 40 ml of cold water, then add 5 ml of hydrochloric acid (sp. gr. 1.18), filter and dilute to 50 ml. (10 ml of this solution contains approximately 200 mg of aluminium ions.) Alternatively, dissolve 1 g of aluminium (99.99%) in hydrochloric acid (sp. gr. 1.18) and dilute to 50 ml.

Ammonia solution (sp. gr. 0.880).

Ammonia solution (2:1).

Ammonium acetate (20% w/v). Dissolve 200 g of ammonium acetate in one litre of water.

Ammonium nitrate (2% w/v). Dissolve 20 g of ammonium nitrate in one litre of water, add a few drops of methyl red indicator (see below), then add ammonia solution (2:1) until the indicator just turns yellow.

Ammonium nitrate (acidified) (2% w/v). Dissolve 20 g of ammonium nitrate in one litre of water, add a few drops of Mixed Indicator (see below), followed by sufficient nitric acid (sp. gr. 1.42) to turn the indi-

cator violet, then add ammonia solution (2:1) until the indicator just turns green, indicating a pH of 3.4.

Ammonium oxalate (0.1% w/v). Dissolve 1 g of ammonium oxalate in one litre of water.

Bromine water (saturated solution). Pour a small quantity of bromine into a bottle containing 200 ml of water, carrying out the operation in an efficient fume cupboard to prevent any bromine vapour being inhaled. Stopper the bottle and shake at intervals until a saturated solution is obtained.

Bromo-phenol blue indicator. Dissolve 40 mg of the free acid in 1.2 ml of sodium hydroxide solution (N/20), dilute to 100 ml with water and filter.

2:2'-Dipyridyl (0.1% w/v). Dissolve 0.1 g of the reagent in water containing 2.0 ml of hydrochloric acid (N/1) and dilute the solution to 100 ml with water.

Diethyl ether.

Ethanol.

Hydrochloric acid (sp. gr. 1.18).

Hydrochloric acid (1:1).

Hydrochloric acid (1:4).

Hydrochloric acid (1:99).

Hydrochloric acid (N/1).

Hydrofluoric acid (40% w/w).

Hydrofluoric acid (40% w/w, Fe ≤ 0.00005%).

Hydrogen peroxide (100 vols).

Hydrogen sulphide (washed).

Hydrogen sulphide wash solution. Pass hydrogen sulphide gas into hydrochloric acid (1:99) until the solution is saturated.

Hydroxylamine hydrochloride (10% w/v). Dissolve 10 g of hydroxylamine hydrochloride in water, filter if necessary and dilute to 100 ml.

Lead chlorofluoride wash solution. Dissolve 10 g of lead nitrate in 200 ml of water, and add this to a solution containing 1 g of sodium fluoride and 2 ml of hydrochloric acid (sp. gr. 1.18) in 100 ml of water. Mix thoroughly and allow the precipitate to settle. Decant the supernatant liquid and wash the precipitate five times by decantation with 200 ml portions of water. Finally add one litre of water to the precipitate and shake the mixture at intervals over a period of one hour. When required for use, filter the supernatant liquid through a sintered glass crucible of porosity Grade No. 4 or a 'close' paper. Further quantities of wash solution may be prepared by treating the residual precipitate with fresh portions of water.

Methyl orange indicator. Dissolve 50 mg of methyl orange in 100 ml of water.

Methyl red indicator. Dissolve 25 mg of the sodium salt of methyl red in 100 ml of water.

Mixed Indicator. Dissolve 50 mg of methyl orange in 50 ml of ethanol. Dissolve 50 mg of methylene blue in 50 ml of ethanol. Mix the two solutions.

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Nitric acid (sp. gr. 1.42).

Nitric acid (1:4).

Perchloric acid (sp. gr. 1.54) (60% w/w).

Sodium chloride (10% w/v). Dissolve 10 g of sodium chloride in water and dilute to 100 ml.

Sodium cobaltinitrite. Transfer 12 g of cobalt nitrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), 24 g of sodium nitrite and 10 ml of acetic acid (glacial) to a filter flask and add water to give a total volume of about 100 ml. Warm the solution to dissolve the salts and heat almost to boiling. Attach the flask to a suction pump and apply suction for one hour to remove oxides of nitrogen. Filter the cold solution through a sintered glass crucible of porosity Grade No. 4 and use the same day. These quantities are sufficient for four determinations.

Sodium hydroxide (N/1).

Sodium zinc uranyl acetate in alcohol wash solution (U). Transfer 475 ml of ethanol* and 25 ml of water to a flask of about one litre capacity. Add 1 g of sodium zinc uranyl acetate, then heat the flask and contents carefully to about 60°C and shake to mix them thoroughly. Cool the solution and allow it to stand for at least 24 hours. When required for use, ensure that the solution is at room temperature and filter through a sintered glass crucible of porosity Grade No. 4 or a 'close' paper immediately before use.

Sulphuric acid (1:1).

Sulphuric acid (1:4).

Sulphuric acid (1:9).

Sulphuric acid (5:95).

Zinc nitrate. Dissolve 10.0 g of zinc oxide in 100 ml of nitric acid (1:4) immediately before use.

Zinc uranyl acetate. Transfer 100 g of uranyl acetate ($\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$) and 300 g of zinc acetate ($\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$) to a flask of about two litres capacity. Dilute 27 ml of acetic acid (glacial) to 100 ml with water, pour the diluted acid into the flask and add a further 800 ml of water. Shake the flask to ensure thorough mixing and heat the mixture just to boiling to effect solution of the salts. Add 0.1 g of sodium chloride, shake the flask well to dissolve the sodium chloride, set aside to cool, and allow to stand for at least 24 hours. When required for use ensure that the solution is at room temperature and filter through a sintered glass crucible of porosity Grade No. 4, or a 'medium' paper immediately before use.

Solid reagents. Ammonium sulphate. Lead nitrate.

Oxalic acid. Potassium carbonate (anhydrous). Sodium acetate (hydrated). Sodium carbonate (anhydrous).

Standard solutions

Iron solution. Prepare the standard solution, containing the equivalent of 0.1 g of ferric oxide (Fe_2O_3) per litre, from ferrous ammonium sulphate,† by dissolving 0.4911 g of $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ in 100 ml of sulphuric acid (1:9), and diluting to one litre with water.

Prepare the dilute standard iron solution *E*, containing the equivalent of 0.01 mg of Fe_2O_3 per ml, by diluting 10 ml of the strong solution to 100 ml with water immediately before use.

Titanium solution. Prepare the standard solution, containing the equivalent of 0.1 g of titanium oxide (TiO_2) per litre, from potassium titanium oxalate.† Weigh 0.4433 g of potassium titanium oxalate ($\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$) into a Kjeldahl flask, add 1 g of ammonium sulphate and 100 ml of sulphuric acid (sp. gr. 1.84). Gradually heat the mixture to boiling and boil for 10 minutes. Cool, pour the solution slowly into 750 ml of cold water, in a heat-resisting beaker or flask, stirring well. Allow to cool before diluting to one litre in a volumetric flask (Solution *F*).

Filter papers

Filter papers should be of the 'ashless' type and the following designation is used:

'Open.' The grade generally used by analysts for filtering aluminium hydroxide or large amounts of silica.

'Medium.'

'Close.' The grade generally used by analysts for filtering barium sulphate.

Glassware

Glassware should be of chemically resistant quality and all new apparatus should be cleaned before use. Recommended procedures are:

For beakers, conical flasks, etc., boil with nitric acid (sp. gr. 1.42), hydrochloric acid (sp. gr. 1.18), and finally with water.

For volumetric ware, reagent bottles, etc., fill with hydrochloric acid (1:1), ensuring that all ground glass surfaces are covered, and allow to stand for at least 30 minutes before washing thoroughly with water.

Analytical procedures

Determination of silica

Weigh 1.0 g of the prepared sample into a 175 ml

* Ethanol may be replaced by industrial methylated spirit (ethanol containing 5% by volume of approved wood naphtha) of equivalent strength. It should be noted that the use of industrial methylated spirit is governed by the Methylated Spirits Regulations 1952 (S.I. 1952 No. 2230).

† A bottle of the reagent may be tested for purity and if satisfactory carefully stored and used only for the preparation of the standard solution.

platinum dish and add 1.3 g of anhydrous sodium carbonate. Mix intimately using the smooth end of a glass rod. Ease the mixture into the centre of the dish, flatten the charge so that it covers an area about 3 cm in diameter and then cover it as uniformly as possible with an additional 0.7 g of the sodium carbonate, cleaning the rod with some of the carbonate and brushing the last trace into the dish. Heat the dish and contents gently at first and finally to a temperature of 950°C in a muffle furnace, discontinuing the heating when fusion is complete. Remove the dish from the furnace, and cover it to prevent loss during cooling.

To the cooled, covered melt, add 10 ml of aluminium chloride solution, then 40 ml of hydrochloric acid (1:1), and allow the mixture to digest on the steam-bath until the melt is completely disintegrated, hastening the action of the acid by occasionally detaching the crust of insoluble matter which tends to cover and protect the inner portions of the melt, but take care that spitting does not occur. When disintegration is complete, remove the cover, wash the under-surface with hot water and allow the washings to go into the dish. Crush all particles of solid matter with the smooth end of the glass rod. Evaporate the mixture to dryness on the steam-bath, breaking up the mass from time to time to aid the escape of vapour. Cool, drench the residue with 5 ml of hydrochloric acid (sp. gr. 1.18) and 20 ml of warm water. Cover the dish and digest the contents on the steam-bath for 10 minutes and filter through an 11 cm 'open' paper. Wash the insoluble matter by decantation twice with hot hydrochloric acid (1:99), several times with hot water, then gradually transfer it to the paper, using a jet of hot water. Wash the precipitate with hot water until free from chloride. Transfer the paper and precipitate (*S*) to an ignited, weighed* platinum crucible with lid.

Return the filtrate and washings to the platinum dish and evaporate to dryness on the steam-bath. Heat the residue at 110°C for 15 minutes in an air-oven. Cool and drench the residue with 5 ml of hydrochloric acid (sp. gr. 1.18), rinse down the inner walls of the dish with 20 ml of hot water and stir the contents. Cover the dish and digest on a steam-bath for 10 minutes. Filter the solution through a 9 cm 'close' paper, wash the small silica residue twice with hot hydrochloric acid (1:99) and transfer it to the paper, using a jet of hot water. Continue washing with hot water until free from chloride. Place the paper and precipitate in the crucible with the main silica precipitate (*S*), partly cover the crucible and heat, gently at

first and then at approximately 600°C until free from carbon. Finally cover the crucible, ignite the precipitate at 1200°C for 30 minutes, cool over a good desiccant and weigh while still covered. Repeat the ignition until constant weight is attained (W_1). Moisten the ignited impure silica with water, add 10 ml of hydrofluoric acid (40% w/w) and 6 drops of sulphuric acid (1:1). Evaporate the more volatile constituents, drive off the sulphuric acid by subsequently heating the crucible on a hot-plate, then cautiously heat over a free flame, cover and finally ignite at 1200°C for 2 minutes. Cool in a desiccator and weigh while still covered. Repeat the ignition until constant weight is attained (W_2). The difference between the weights (W_1 and W_2) represents the weight of silica.

From the weight of silica thus determined, calculate and report the percentage silica (SiO_2) in the sample.

Determination of zinc, aluminium, and calcium oxides

Weigh 1.0 g of the prepared sample into a small (100 ml) platinum dish. Moisten with water, add 15 ml of hydrofluoric acid (40% w/w) and either gently swirl the contents of the dish or stir with a platinum wire to assist decomposition. Add 2 ml of sulphuric acid (1:1) and evaporate gently until a syrupy mass remains. Increase the heat and continue the evaporation until copious fumes of sulphuric acid appear. Cool the dish and contents, rinse the walls of the dish with water, add a few drops of nitric acid (sp. gr. 1.42) and continue the evaporation until the excess of acid is removed and the residue is dry. Cool the dish, add 10 ml of hydrochloric acid (1:1), heat until all soluble matter has dissolved† and then wash the contents of the dish into a 250 ml beaker, using hot water, the final volume being about 100 ml. Heat the solution, pass hydrogen sulphide gas for 20 minutes and allow to stand warm for one hour.‡ Filter the solution through an 11 cm 'close' paper, washing the paper well with hydrogen sulphide wash solution. Retain the filtrate and washings (solution *H*) and discard the precipitate.

Determination of zinc oxide

Boil the solution (*H*) until all hydrogen sulphide has been removed. Dilute to approximately 300 ml, cool, add 5 g of ammonium sulphate followed by about 10 drops of Mixed Indicator and then add ammonia solution (2:1) dropwise and with stirring until the indicator just changes to green.§ Heat the solution to 60°C and pass hydrogen sulphide gas for 20 minutes. Stand the beaker and contents on a steam-bath for 30

* This weight is not used in the actual calculation of silica but if the difference between it and W_2 is greater than 5 mg then it is an indication that the silica precipitate was unduly contaminated and the final result should be viewed with suspicion.

† Any trace of barium present will be removed during the filtration of the Group II precipitate.

‡ This procedure is precautionary for the removal of traces of certain Group II elements.

§ The indicator is violet at pH 3.2 and green at pH 3.4.

minutes. Stir paper pulp into the solution and filter through a 'medium' paper, transferring the contents of the beaker completely to the paper with hot ammonium nitrate (acidified) solution. Continue washing the precipitate until free from chloride. Reserve the filtrate (Z). Place the paper and precipitate in an ignited, weighed silica or porcelain crucible. Dry the paper, heat at a low temperature until all carbon is removed, and then ignite at 800°C for one hour. Cool the covered crucible in a desiccator and weigh. Repeat the ignition until constant weight is attained.

From the weight of zinc oxide obtained, calculate and report the percentage of zinc oxide (ZnO) in the sample.

Determination of aluminium oxide

Acidify the filtrate (Z) with a few drops of hydrochloric acid (sp. gr. 1.18) and boil the solution for 15 minutes to remove hydrogen sulphide. Add 2 ml of hydrogen peroxide and continue boiling for 30 minutes, concentrating to approximately 200 ml.

Whilst the solution is near to boiling add ammonia solution (2:1) dropwise with constant stirring, until the additional drop momentarily gives a precipitate (indicating that the solution is almost neutral), then add 3 drops of methyl red indicator. Continue the addition of ammonia solution (2:1) dropwise and with stirring, until the indicator just changes to yellow. Boil for 1 minute, allow to settle and then filter the solution through a 9 cm 'open' paper. Wash the precipitate three times with hot ammonium nitrate solution. Retain the filtrate (A). Dissolve the precipitate on the paper in hydrochloric acid (1:1), collecting the solution in the original beaker. Reprecipitate the hydroxides with ammonia solution (2:1) as above. Filter the solution through a 9 cm 'open' paper, transferring all the precipitate to the paper using hot ammonium nitrate solution. Continue washing the precipitate until free from chloride. Place the paper and precipitate (R) in an ignited, weighed platinum crucible with lid.

Combine the filtrate with filtrate (A), make slightly acid with hydrochloric acid (sp. gr. 1.18) and concentrate to 100 ml. Boil the solution, then add ammonia solution (2:1) dropwise and with stirring, until the indicator just changes to yellow. Keep the solution just below boiling point for 10 minutes ensuring that it remains faintly ammoniacal. Filter the solution through a 9 cm 'close' paper, transferring the small precipitate completely to the paper, using hot ammonium nitrate solution. Continue washing the precipitate until free from chloride. Retain the filtrate (C). Place paper and precipitate in the crucible with the main hydroxides (R), dry and heat at a low temperature until all carbon is removed, then ignite the covered crucible at 1200°C for 30 minutes. Cool the covered crucible in a desiccator

and then weigh. Repeat the ignition until constant weight is attained.

From the weight of 'R₂O₃' obtained, calculate the percentage in the sample. Subtract the values subsequently obtained for the percentages of ferric oxide (Fe₂O₃) and titanium oxide (TiO₂) and report the difference as the percentage aluminium oxide (Al₂O₃) in the sample.*

Determination of calcium oxide

Acidify the filtrate (C) with hydrochloric acid (sp. gr. 1.18) and concentrate the solution to 150 ml. Add 2 drops of methyl red indicator and 1 g of oxalic acid. Heat the solution to boiling and add ammonia solution (2:1) dropwise until the solution is just alkaline. Stand the beaker and contents on a steam-bath for one hour, maintaining the slight alkalinity, then cool the solution to room temperature. Filter off the precipitate on a 9 cm 'close' paper, and wash it three times with ammonium oxalate solution. Discard the filtrate.

Dissolve the precipitate in 10 ml of hot hydrochloric acid (1:1) and collect the solution in the original beaker. Dilute to 150 ml, add 0.2 g of oxalic acid and 2 drops of methyl red indicator. Heat the solution to boiling, add ammonia solution (2:1) dropwise until the solution is just alkaline and allow to stand as before. Filter the cold solution through a 9 cm 'close' paper, transferring all the precipitate to the paper using ammonium oxalate solution. Continue the washing until the precipitate is free from chloride. Discard the filtrate.

Place the paper and precipitate in an ignited, weighed platinum crucible with lid. Dry the paper and heat at a low temperature until all carbon is removed. Cover the crucible with a lid and ignite at 1200°C for 5 minutes. Transfer the crucible to a desiccator, replacing the lid, and weigh as soon as cold. Repeat the ignition until constant weight is attained.

From the weight of calcium oxide obtained, calculate and report the percentage of calcium oxide (CaO) in the sample.

Determination of sodium oxide

Weigh 0.1 g of the prepared sample into a small (100 ml) platinum dish. Moisten with water, add 5 ml of hydrofluoric acid (40% w/w) and either gently swirl the contents of the dish or stir with a platinum wire to assist decomposition. Add 10 drops of perchloric acid and evaporate gently until a syrupy mass remains. Increase the heat and continue the evaporation until fumes of perchloric acid cease and the mass is dry. Remove the dish from the source of heat as soon as the

* Any ZrO₂ present would be included in the calculated Al₂O₃ result. The ZrO₂ content of this glass, however, is negligible.

contents are dry, otherwise the perchlorates may be decomposed and solution of the residue may be difficult.

Dissolve the residue in 1 ml of hydrochloric acid (1:4), warming if necessary, then cool. Add 20 ml of zinc uranyl acetate solution and thoroughly mix the contents by gentle stirring for 1 to 2 minutes. Allow the dish and contents to stand at room temperature (about 20°C) for 45 minutes and keep the zinc uranyl acetate stock solution and the alcoholic sodium zinc uranyl acetate wash solution (*U*) at the same temperature.

Wash a sintered glass crucible, porosity Grade No. 4, with water, then three times with ethanol and finally twice with 10 ml portions of diethyl ether. Maintain suction throughout and continue until no further smell of ether can be detected. Carefully wipe the crucible with a dry, fluffless cloth and leave in the balance-case for 30 minutes, then weigh.

Meanwhile, transfer 20 ml of zinc uranyl acetate solution to a small wash bottle and about 20 ml of the wash solution (*U*) to a similar bottle. Filter off the precipitated sodium zinc uranyl acetate from the sample solution, transferring completely to the weighed, sintered glass crucible, using small volumes of the reagent solution. Allow the crucible to drain, wash it four times with the alcoholic wash solution (*U*) and then twice with 10 ml portions of diethyl ether. Maintain suction throughout and continue until no smell of ether remains. Wipe the crucible with a dry, fluffless cloth, leave in the balance-case for 30 minutes, then weigh. Leave the crucible in the balance-case and reweigh at intervals until constant weight is attained. Carry out a blank determination on the reagents used.

From the corrected weight of sodium zinc uranyl acetate ($\text{NaC}_2\text{H}_3\text{O}_2 \cdot \text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 6\text{H}_2\text{O}$) calculate and report the percentage sodium oxide (Na_2O) in the sample.

Weight of precipitate $\times 0.02015 =$ Weight of Na_2O .

Determination of potassium oxide

Weigh 0.5 g of the prepared sample into a small (100 ml) platinum dish. Moisten with water, add 10 ml of hydrofluoric acid (40% w/w) and either gently swirl the contents of the dish or stir with a platinum wire to assist decomposition. Add 10 drops of nitric acid (sp. gr. 1.42), 2 ml of perchloric acid, and evaporate gently until a syrupy mass remains. Increase the heat and continue the evaporation until fumes of perchloric acid cease and the mass is dry, then immediately remove the dish from the source of heat.

Cool the residue, add 10 ml of water and 1 ml of hydrochloric acid (sp. gr. 1.18). Warm to obtain complete solution, then evaporate on the steam-bath to a volume of about 2 ml. Add 25 ml of sodium cobaltinitrite solution and evaporate the mixture to a thick

syrup on a steam-bath. Remove the dish, cool and add 25 ml of acetic acid (5:95), stirring the mixture at intervals until all soluble salts have dissolved.

Filter off the precipitated sodium potassium cobaltinitrite on a weighed, sintered glass crucible of porosity Grade No. 4, previously cleaned and dried at 110°C, transferring the precipitate completely to the crucible, using acetic acid (5:95). Wash a further five times with the acetic acid and once with cold water. Dry the crucible and precipitate at 110°C for one hour, cool in a desiccator and weigh. Repeat the drying until constant weight is attained. Carry out a blank determination on the reagents used.

From the corrected weight of the sodium potassium cobaltinitrite ($\text{NaK}_2\text{Co}(\text{NO}_2)_6 \cdot \text{H}_2\text{O}$) calculate and report the percentage of potassium oxide (K_2O) in the sample.*

Weight of precipitate $\times 0.2074 =$ Weight of K_2O .

Determination of fluorine

Weigh 1.5 g of the prepared sample into a small (100 ml) platinum dish and add 6.0 g of anhydrous potassium carbonate. Mix intimately using the smooth end of a glass rod, brushing into the dish any material adhering to the rod. Cover the dish with a platinum lid and heat the mixture, gently at first and finally at 900–1000°C for 5 minutes in a muffle furnace to produce a clear melt. Avoid prolonged heating. Remove the dish from the furnace and allow to cool.

To the cooled melt, add about 50 ml of hot water and allow the mixture to digest on a steam-bath until disintegration is complete (40–60 minutes). Rinse the cover with hot water, collecting the washings in the dish and filter the solution through an 'open' paper in a Büchner funnel. Wash the paper and insoluble residue six times with hot water, allowing the precipitate to drain almost to dryness after each wash. Transfer the filtrate to a 400 ml beaker, dilute to about 150 ml and add, with constant stirring, 20 ml of zinc nitrate solution. Heat the mixture to boiling and boil for 1 minute, stirring continuously to avoid 'bumping'.

Filter the hot solution through a 7 cm 'close' paper in a Büchner funnel and wash the paper and precipitate six times with hot water, allowing the precipitate to drain almost to dryness after each wash. Transfer the filtrate to a 600 ml beaker; the volume of the solution at this stage should be about 250 ml. Add 3.0 ml of sodium chloride solution, 2 drops of bromo-phenol blue indicator, and add nitric acid (1:4) carefully until the indicator just changes to yellow. Boil the solution for 2 minutes to remove any dissolved carbon dioxide.

* When the potassium oxide is 1% or more it is advisable to dissolve the precipitate in hydrochloric acid and convert to perchlorate.

Cool the solution to about 70°C, add 2.0 ml of hydrochloric acid (1:1), 5.0 g of solid lead nitrate, and stir to dissolve the salt. When solution is complete add 5.0 g of solid sodium acetate and stir vigorously to promote the precipitation of lead chlorofluoride. Stand the beaker on a steam-bath for 30 minutes, occasionally stirring the contents, then allow to stand cold overnight.

Filter off the precipitate on a weighed, sintered glass crucible, porosity Grade No. 4 (previously dried at 150°C), allow the crucible to drain dry, then wash the beaker, crucible, and precipitate once with cold water. Use the lead chlorofluoride wash solution to transfer to the crucible any precipitate still adhering to the beaker, then wash the precipitate six times with the wash solution and finally twice with cold water. Dry the crucible and precipitate at 150°C for 90 minutes, cool in a desiccator and weigh. Repeat the drying until constant weight is attained.

From the weight of lead chlorofluoride (PbClF) obtained, calculate and report the percentage fluorine (*F*) in the sample.

Weight of PbClF \times 0.07263 = Weight of *F*.

Determination of total iron (expressed as ferric oxide)

Prepare a 'blank' solution concurrently with the sample solution.

Weigh 0.1 g of the prepared sample into a small platinum dish or crucible, specially cleaned to be free from iron. Moisten with water, add 5 ml of hydrofluoric acid (40% w/w, Fe \leq 0.00005%), and either gently swirl the contents of the dish or stir with a platinum wire to assist decomposition. Add 1 ml of sulphuric acid (1:1), evaporate gently almost to dryness, then increase the heat and continue the evaporation until fumes of sulphuric acid cease. Cool the dish and contents and add a further 1 ml of sulphuric acid (1:1) and again heat until fumes of sulphuric acid cease and the residue is dry. Add 10 ml of hydrochloric acid (1:4) to the residue and warm to obtain a clear solution.

Transfer the solution to a 200 ml beaker, rinsing the dish with warm water, and adding the washings to the beaker. Add 1 drop of methyl orange and neutralize the solution by the addition of sodium hydroxide (N/1). Add 2 ml of hydrochloric acid (N/1) to the solution, followed by a few drops of bromine water to destroy the indicator colour, then boil the solution until colourless, thus removing the excess of bromine. Cool the solution, and transfer to a 100 ml volumetric flask. The volume at this stage should be approximately 50 ml.

Add 2 ml of hydroxylamine hydrochloride, swirl to mix and allow to stand for 1 minute. Then add 10 ml of ammonium acetate, mix and add 5 ml of 2:2'-

dipyridyl. Dilute to 100 ml with water, and mix thoroughly.

Measure the difference in optical density between the sample and the blank solutions using either (1) a spectrophotometer at a wavelength of 520 m μ or (2) an absorptiometer with Ilford Spectrum Green 604 or equivalent filters. From the appropriate calibration graph determine the amount of ferric oxide equivalent to the difference obtained. From this weight calculate and report the total iron as percentage of ferric oxide (Fe₂O₃) in the sample.

Calibration graph for iron. Transfer known volumes of the diluted standard iron solution (*E*) covering the range 0 to 0.15 mg Fe₂O₃ to a series of 100 ml volumetric flasks. To each solution add 2 ml of hydrochloric acid (N/1) and dilute to about 50 ml. Then add 2 ml of hydroxylamine hydrochloride, mix and allow to stand for 1 minute; add 10 ml of ammonium acetate then 5 ml of 2:2'-dipyridyl. Dilute to 100 ml with water and mix thoroughly. Measure the difference in optical density between the solution with no added iron and each of the other solutions using either (1) a spectrophotometer at a wavelength of 520 m μ or (2) an absorptiometer with Ilford Spectrum Green 604 or equivalent filters. For most instruments a 4 cm cell will be suitable. Plot the differences in optical density against the concentration (in mg Fe₂O₃) to give the calibration graph.

Determination of titanium oxide

Prepare a 'blank' solution concurrently with the sample solution.

Weigh 2.0 g of the prepared sample into a small (100 ml) platinum dish. Moisten with water, add 20 ml of hydrofluoric acid (40% w/w) and either gently swirl the contents of the dish or stir with a platinum wire to assist decomposition. Add 4 ml of sulphuric acid (1:1) and evaporate gently until a syrupy mass remains. Increase the heat and continue the evaporation until the residue is almost dry. Cool the dish and contents, wash down the walls of the dish with 2 ml of sulphuric acid (1:1), and again evaporate almost to dryness. Again cool the dish and contents, wash down the walls of the dish with 2 ml of sulphuric acid (1:1) and evaporate almost to dryness.*

Add 25 ml of sulphuric acid (1:4) to the cold residue, warm and transfer completely to a 200 ml beaker using as small a volume as possible of sulphuric acid (5:95) to clean the dish. Boil gently to dissolve all soluble material. Cool, and, if necessary, filter through a sintered glass crucible, porosity Grade No. 4, or a 9 cm 'close' paper, washing the residue with sulphuric acid

* All traces of fluorine must be removed since this seriously interferes with the determination.

(5:95). Transfer the filtrate to a 100 ml volumetric flask, dilute to the mark with sulphuric acid (5:95), and mix.

Transfer a 50 ml aliquot of this solution to a dry flask, add 1 ml of hydrogen peroxide and mix. Using the remainder of the solution as reference solution measure the optical density using either (1) a spectrophotometer at a wavelength of 420 m μ or (2) an absorptiometer with Ilford Spectrum Violet 601 or equivalent filters.

Treat the 'blank' solution in a similar manner and apply a correction if necessary. From the appropriate calibration graph determine the amount of titanium oxide. Calculate and report the percentage of titanium oxide (TiO₂) in the sample.

Calibration graph for titanium. Transfer known volumes of the standard titanium solution (F) covering the range 0.2 to 2 mg TiO₂, to a series of 50 ml volumetric flasks. To each solution add 5 ml of sulphuric acid (1:1), dilute to 50 ml with water, add 1 ml of hydrogen peroxide and mix. Prepare a series of similar solutions, but without the addition of hydrogen peroxide, to be used as reference solutions.

Measure the optical density of the standard solutions, using the appropriate reference solutions with either (1) a spectrophotometer at a wavelength of 420 m μ or (2) an absorptiometer with Ilford Spectrum Violet 601 or equivalent filters. For most instruments a 4 cm cell will be suitable. Plot the differences in optical density against the concentration (in mg TiO₂) to give the calibration graph.

Determination of boric oxide

This may be determined by the method of G. R. Ball & E. W. Fajans (*J. Soc. Glass Tech.*, 1951, 35, 93 T).

Loss on ignition at 550° C

Grind a sample of glass, as described under *Preparation of the sample* on page 10, dry at once at 110° C for one hour, transfer to a desiccator and as soon as cold quickly weigh approximately 1.0 g into an ignited, weighed platinum crucible. Heat the crucible and contents, with the lid lightly in position, in an electric muffle furnace at a temperature of 550° C for one hour. Cool in a desiccator and weigh quickly. From the loss in weight calculate the percentage loss at 550° C.