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Combustion separation techniques in glass analysis

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The combustion method is suitable for the separation and determination of volatile components of glass. Details of fluorine, boron, sulphur and chloride in glass as well as carbon and sulphur in sand. Comparison with other methods demonstrates the efficiency of the combustion method.

Procédé de séparation par combustion dans l'analyse des verres

La méthode par combustion est parfaitement appropriée à la séparation et au dosage des composants volatils du verre. On décrit en détail la méthode et l'appareillage utilisés et l'on fournit les résultats de dosages de fluor, de bore, de soufre et de chlorure dans le verre ainsi que ceux de dosages de carbone et de soufre dans les sables. La comparaison avec d'autres techniques analytiques montre l'intérêt du procédé par combustion utilisé.

Verbrennung als Trennungsmethode bei der Glasanalyse

Die Verbrennungsmethode ist für die Abtrennung und Bestimmung der flüchtigen Glaskomponenten gut geeignet. Es werden eingehend Einzelheiten der eingesetzten Verfahren und Geräte beschrieben und Ergebnisse von Fluor-, Bor-, Schwefel-, Chloridbestimmungen in Glas sowie von Kohlenstoff- und Schwefelanalysen an Sanden mitgeteilt. Vergleiche mit anderen Analysenmethoden beweisen die Leistungsfähigkeit des angewendeten Verbrennungsverfahrens.

Combustion separation techniques for analysing glasses are not new; Adams and Williams [1] in 1958 reported a method for determining fluorine in opal glasses and other silicate materials and Cluley [2] in 1961 published a paper in which "it was hoped that some relaxation of the experimental conditions might be permissible for the more limited objective of determining fluorine in one type of opal glass". This method did, indeed, replace the conventional lead chloro-fluoride procedure for control purposes, and was claimed to have a standard deviation of 0,02% at about the 5% fluorine level.

A consideration of the procedure, in which the sample is heated with an accelerator in a stream of steam and the volatilised fluorine is condensed as hydrofluoric acid, suggests that constituents which can be separated in this manner should be capable of very precise determination. For example, there are no stages at which filtration or transference of precipitates are necessary and so the possibilities of analytical errors accumulating at such stages are eliminated. In this report, therefore, the intention is to show how the combustion separation technique has been exploited in determining volatile constituents of glasses and of sand.

1. General

The essential feature of an assembly for determining fluorine is the tube furnace — in this case a twin tube furnace so that duplicate determinations can be done simultaneously. This particular furnace is capable of temperatures up to about 1500 °C and is heated by silicon carbide electrodes. Then, by varying the apparatus and carrier gas supplies, as will be seen later, it can be used to separate not only fluorine, but boron, sulphur and chloride from glass and the very small amounts of carbon and sulphur from glass-making sands. All of these determinations will be discussed in this report.

2. The determination of fluorine

The authors mentioned earlier, Cluley in 1961 and Adams and Williams in 1958 have already published reports on the development of this technique and so very little reference need be made here. It should be sufficient to show from Figure 1 the detail of the procedure used.

The sample, mixed with an accelerator, in this case V_2O_5, is placed in a platinum boat (I) and pushed into a fused silica combustion tube (G) in the tube furnace (H). The end of the tube is closed (F) and steam, from a steam-generator (B), is passed through the tube, over the sample and is condensed and collected in a flask (N) at the other end of the furnace. The furnace temperature is raised to 1050 °C and heating is continued for about 40 minutes or until about 120 ml of distillate has been collected. The fluorine content of the sample is then determined on the distillate, by the thorium nitrate titration method. Quite clearly other methods, such as colorimetry, could be used to measure the fluorine, which is distilled over as hydrogen fluoride. There appears to be no adverse effects in using silica combustion tubes and glass condensers here, possibly because the hydrogen fluoride is heavily diluted with steam and is in contact with the silicate material for only very short periods of time.

Temperature appears to be the most important factor; for opal glasses the process is much more rapid at 1000 °C than at 900 °C and is even more rapid and complete at 1050 °C. Fineness of the sample powder and ratio of sample to accelerator seem not to be important, within certain limits — about five parts of V_2O_5 to one part of sample has been shown to be suitable — and other chemicals than V_2O_5 can be used as accelerator. U_3O_8, WO_3 and Al_2O_3 have all been used satisfactorily.

Table 1 shows the results obtained by this procedure using S.G.T. standard glass No. 4. The published value for this glass is 4,96% F — obtained by the lead chloro–fluoride precipitation method — with a s. d. of 0,10%. The results obtained show a mean value in good agreement with the published figure and the standard deviation of 0,02% — although a within-laboratory value, compares favourably with the published between-laboratory value of 0,10%.

In some combustion methods for analysing steels and slags a porous refractory capsule is used to contain the sample. It is claimed that better heat transfer throughout the sample is obtained and so this modification was tried for glass analysis. These capsules, or cartridges as they are called, are inexpensive, are about 50 mm long by about 10 mm o. d., are used only once and certainly obviate the necessity of cleaning out the platinum boat. They were used to contain the samples from which the results in Table 1 were obtained. Because of this claim of better heat transfer some results were obtained using these cartridges but omitting the accelerator and these are shown in Table 2. This shows that heat alone is not sufficient to completely separate the fluorine from the glass — the mean value is about 0,2% below the published mean — and that a much greater variability is achieved. The omission of the accelerator, therefore, is not advisable.

3. The determination of boric oxide

Next, the determination of boric oxide in glass and here again the experimental development work has been described fully in the literature. The assembly is essentially the same as that for fluorine shown in Figure 1. The carrier gas is again steam but the furnace temperature in this case is raised from 1100 °C to 1450 °C over a period of one hour and whilst about 150 ml of distillate are collected. At such temperatures it is not practical to use a fused silica combustion tube so an aluminous porcelain or platinum combustion tube is substituted. Aluminous porcelain tubes are rather fragile and need to be handled carefully; thermal shocks need to be avoided, especially when cooling down after a determination.

Boric oxide from the sample is extracted into the steam and collected in the receiver as boric acid. Any suitable finish can be applied but the conventional sodium hydroxide titration method, using mannitol, has been shown to be satisfactory.

Table 3 shows the results obtained on S.G.T. standard glass No. 2, which has a published mean value of 12,86% and s. d. of 0,06% obtained by the modified Wherry method. By pyrohydrolysis the mean value is slightly higher, at 12,91% but this is a within-laboratory result compared with the published value which is a between-laboratory result. A glass similar in composition to glass No. 2 has been analysed by the conventional method and by the combustion method and the results are shown in Table 4. Here it can be seen that, within-laboratory values for the mean are almost identical, at 12,33% by combustion and 12,32% by conventional, and the s. d.'s are the same at 0,03%. Based on this evidence pyrohydrolysis is now commonly used for boron determinations at this level.

In the conventional method an extra filtration stage must be included when elements such as zinc, lead and phosphorus are present in the glass. Table 5 shows the results obtained by pyrohydrolysis when increasing amounts of these three elements were added to the sample. For zinc it appears that no interference is obtained when up to about 8% of zinc oxide is present; for lead the limit seems to be about 5% and for phosphorus about 5% expressed as the pentoxide. There are, therefore, distinct advantages over the conventional method as well as a saving of about 50% on the time required for a determination.

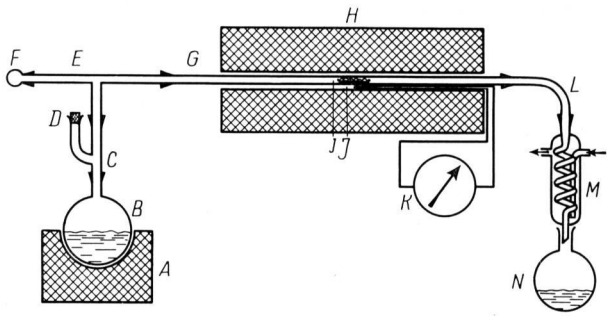

Figure 1. Apparatus for the determinations of fluorine, boron and chloride.

A = mantle heater;
B = 2 dm³ round bottomed flask;
C = multiple adaptor;
D = stopper;
E = T-piece made from one double cone and one cone with plain end;
F = cap;
G = aluminous porcelain combustion tube of length 24 in. and i.d. 0,875 in.;
H = horizontal tube furnace with controller hot zone ≤ 12 in.;
I = platinum combustion boat;
J = thermocouple;
K = pyrometer;
L = plain bend;
M = spiral condenser;
N = 350 cm³ flask receiver.

Table 1. Determination of fluorine using S.G.T. standard glass No. 4
(values in %)

4,95		published value
4,97	mean = 4,97	mean = 4,96
4,98		
5,00	s. d. = 0,02	s. d. = 0,10
4,96		

Table 2. Determination of fluorine withouth accelerator using S.G.T. standard glass No. 4
(values in %)

4,85		
4,45		published values
4,99	mean = 4,74	mean = 4,96
4,72		
4,89	s. d. = 0,21	s. d. = 0,10
5,06		
4,82		
4,82		
5,02		

Table 3. Determination of B_2O_3 using S.G.T. standard glass No. 2

observed results by pyrohydrolysis B_2O_3 in %	mean value in %	s. d. in %	published mean value in %	published s. d. in %
12,96				
12,90				
13,02	12,91	0,07	12,86	0,06
12,86				
12,83				

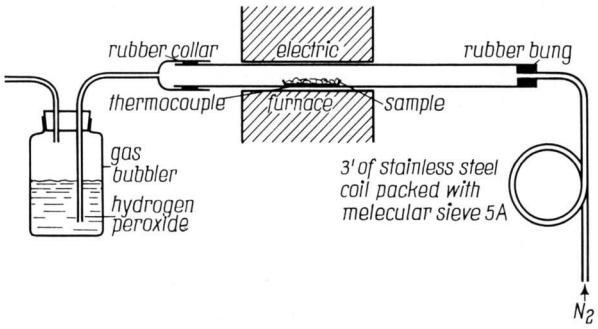

Figure 2. Apparatus for the determination of sulphur.

4. The determination of sulphur in glass

For the determination of sulphur in glass, in this case a soda–lime–magnesia–silica glass, S. G. T. standard glass No. 1 the apparatus is shown in Figure 2. The carrier gas in this case is nitrogen, which is passed through a coil of molecular sieve 5 Å in order to remove any traces of acidic gases. It may be possible to obtain nitrogen which is sufficiently pure to obviate the necessity for this trap and so, in those circumstances it may be omitted. Oxygen has been tried as the sweep gas but a lower order of reproducibility was obtained than with nitrogen.

A number of different accelerators have been examined, including powdered tin, cuprous oxide, ferric oxide and bismuth trioxide — all of which have been advocated in the literature — but complete extraction of sulphur was not achieved with any of them. Consequently the vanadium pentoxide, or preferably uranium octoxide is recommended.

The minimum combustion temperature required is 1400 ° C and the evolved gases are bubbled into an absorbing solution of dilute hydrogen peroxide. After heating for one hour with a gas flow-rate of 0,5 l/h, the absorbing solution is titrated with a standard solution of sodium borate using bromo–cresol green indicator.

The results obtained are shown in Table 6 and it can be seen that they compare very favourably with the published values for this glass. The big advantage of the combustion method over the conventional gravimetric procedure, of course, is the speed. By combustion a result can be abtained in about 1,5 hours compared with more than a working day by the gravimetric method.

5. The determination of chloride in glass

Whilst not a frequently requested analysis the determination of chloride in chloride-refined glasses is sometimes called for. Normally an alkaline fusion of the sample is followed by a water extraction, filtration and titration but the possibility of chloride contamination in many laboratories is quite high. Blank values can also be high and variable, so the possibility of separating the chloride by a combustion process is attractive.

The apparatus used is exactly the same as that used for fluorine determinations, Figure 1. The combustion temperature is also the same, 1050 °C, but chloride is evolved more quickly than fluorine, taking about 25 min or about 100 ml of distillate. The chloride content is determined by measuring the excess of mercury as the mercury diphenyl carbazide complex after combining the chloride as the mercuric salt.

The other halides, fluoride, bromide and iodide do interfere and it is difficult to reduce this interference. However, bromide and iodide are very rare constituents of glasses anyway and if fluoride is present then the total fluoride + chloride and a separate fluoride determination can be done from wich both fluoride and chloride can be calculated.

Table 7 shows the results obtained in testing the reproducibility of the method. Aliquots of a standard sodium chloride solution were dried on to 1 g portions of the accelerator, the mixture was finely ground and then transferred to the combustion boat. Column 1 shows that when sodium chloride equivalent to 0,05 mg of chloride was added the recovery was 0,051 mg with a s. d. of 0,002 mg. Similarly, columns 2 and 3 show that at the 0,10 and 0,20 mg additions the recoveries were 0,098 and 0,199 mg respectively, with s. d.'s of 0,007 and 0,005 mg.

It was not possible to find a glass with a published value for chloride content and so some special melts of

Table 4. Determination of B_2O_3; within-laboratory results

observed results by pyrohydrolysis B_2O_3 in %		mean value in %	s. d. in %	conventional method B_2O_3 in %		mean value in %	s. d. in %
12,36	12,31			12,30	12,30		
12,29	12,35	12,33	0,03	12,35	12,29	12,32	0,03
12,33				12,37	12,32		

Table 5. Determination of B_2O_3; interference by zinc, lead, and phosphate

ZnO added in %	B_2O_3 found in %	PbO added in %	B_2O_3 found i %	P_2O_5 added in %	B_2O_3 found in %
1,00	12,44	1,93	12,40	0,88	12,24
1,73	12,37	4,13	12,24	4,69	12,37
2,40	12,40	4,52	12,23	7,42	12,19
2,80	12,30	7,30	11,90	15,25	12,07
7,90	12,30	12,14	11,82		
		26,41	11,70		

a soda–lime–silica glass were made. Table 8 shows the results obtained from three such glasses and the first salient point is that the recoveries from the second and third glasses are very low compared with the amount added. They are, in fact, about 70% in each case. However, the reproducibility of each set of results is very good indeed, with s. d.'s from 0,004 to 0,006% and it is considered that the analytical procedure is satisfactory. Some further glass melts were made with even higher additions of chloride and this time the recoveries, whilst being somewhat higher at about 80%, were still not satisfactory. The reproducibility was still of a very high order and after examining all the conditions it was considered that variations in furnace atmospheres, temperatures and melting times were probably the cause of variable chloride retentions in the glasses.

6. The determination of carbon in sands

During a laboratory investigation into refining conditions in soda–lime–silica glasses there appeared to be an unexplained variation in the results obtained and it was decided that a determination of the carbon content of the sand being used would be useful. Clearly the carbon content of most sands for making colourless glasses is very low and the conventional gravimetric method, in which the carbon is converted to CO_2 which is then absorbed on to soda asbestos and weighed, would probably lack sensitivity. Accordingly the non-aqueous titration procedure produced by JONES and co-workers [3] was examined and Figure 3 shows the apparatus used.

The finely-ground sample of sand is placed in the boat in the furnace and a stream of oxygen is passed through the system. Small quantities of hydro-carbons in the oxygen must be removed and this is achieved by passing the gas through the U-tube (made of copper) containing platinised asbestos. The lower part of the tube is heated to about 800 °C in an electric burner whilst the top part is kept cool by a water-jacket. The gas then passes through a mixed absorbing column to remove any CO_2, sulphur gases or water produced and the purified oxygen then sweeps through the combustion tube. The sample is heated to 950 °C and the emergent gas stream passes through a second absorbing tower to remove any sulphur gases which may have been generated from the sample itself. The gas is then bubbled through the absorbing solution — a mixture of formdimethylamide and monoethanolamine with thymolphthalein as indicator. CO_2 decolourises the blue solution, converting the amide group to the carboxylic acid group and this is then titrated in situ with tetra-n-butyl ammonium hydroxide back to the blue end-point.

The accuracy and reproducibility were examined by using samples of ignited Loch Aline sand, finely-ground, to which accurately weighed quantities of spectrographically pure carbon powder were added. Table 9 shows the results obtained. The mean value of these results is 0,097% compared with the 0,100% added and the s. d. is about 0,016%. Samples of sand commonly used for making colourless glass were analysed and gave results in the range 0,010 to 0,015%, but determinations on some sands which had been dried in an oilfired drum drier gave results which were a little higher and had some variability.

Table 6. Determination of sulphur using S.G.T. standard glass No. 1

observed results SO_3 in %		mean value in %	s. d. in %	published value in %	published s. d. in %
0,222	0,203				
0,197	0,218				
0,212	0,207	0,214	0,011	0,22	0,01
0,229	0,224				

Table 7. Determination of chloride. Addition of sodium chloride to accelerator sample

for 0,05 mg Cl^- added recovered in mg	for 0,10 mg Cl^- added recovered in mg	for 0,20 mg Cl^- added recovered in mg
0,054	0,096	0,194
0,048	0,097	0,198
0,052	0,092	0,208
0,052	0,094	0,204
0,049	0,110	0,195
mean in mg		
0,051	0,098	0,199
s. d. in mg		
0,002	0,007	0,006

Table 8. Determination of chloride. Sodium chloride added to glass melts

glass (1) added NaCl to give 0,086 % Cl^- content recovered in %	glass (2) added NaCl to give 0,172 % Cl^- content recovered in %	glass (3) added NaCl to give 0,250 % Cl^- content recovered in %
0,073	0,117	0,182
0,085	0,115	0,171
0,080	0,111	0,172
0,083	0,111	0,183
0,084	0,119	0,175
mean in %		
0,081	0,115	0,177
s. d. in %		
0,005	0,004	0,006

Table 9. Determination of carbon in sand

carbon added in %	carbon found in %	
0,100	0,097	0,098
	0,096	0,097
	0,098	0,096
	0,101	0,097
	0,097	
mean in %	0,098	
s. d. in %	0,0014	

7. The determination of sulphur in sands

Continuing the consideration of sand for making colourless glasses there was a suggestion that residues left in the material from floatation separation processes,

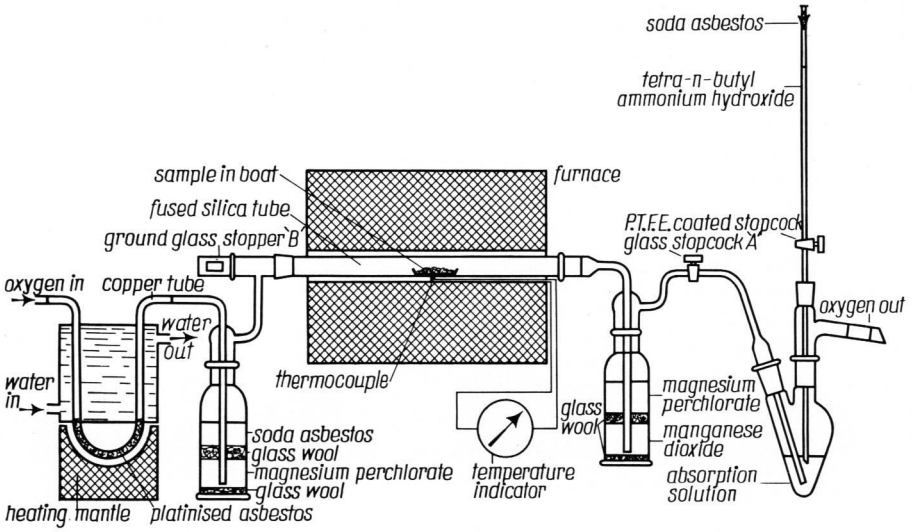

Figure 3. Apparatus for the determination of carbon in sand.

in which some organic sulphonates are used, might conceivably have variable sulphur contents. A method using the apparatus shown in Figure 2 was produced, using a combustion temperature of 950 °C and burning the sulphur off in a stream of purified oxygen. The sulphur gases are collected in a very dilute hydrogen peroxide absorbing solution. Quite clearly the concentration here was too low to permit accurate titration with borax to be made. The addition of a known amount of barium chloranilate to the solution produced a precipitate of barium sulphate and a colour due to chloranilic acid. This colour is measured at 530 nm spectrophotometrically and results in the range 0,002% to 0,011% sulphur have been obtained on beneficiated sands. Calibration is carried out by adding suitable aliquots of a potassium sulphate solution to samples of ignited, finely-ground sand.

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