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The chemical durability of glass: determination of aluminium oxide in extract solutions

(A report by Sub Committee A 2 of the International Commission on Glass)

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Nine laboratories analysed two simulated durability extract solutions containing 1 and 10 ppm Al_2O_3 and one extract solution containing about 0.5 ppm Al_2O_3 using three different methods (chromazurol, eriochrome cyanine and 8-quinolinol). The colorimetric chromazurol method appeared to be the most satisfactory procedure.

La durabilité chimique du verre: dosage de l'alumine dans les solutions

Neuf laboratoires ont analysé deux solutions de synthèse de même composition que celle d'un essai de durabilité et contenant 1 et 10 ppm de Al_2O_3 et une solution contenant environ 0,5 ppm de Al_2O_3 à l'aide de trois méthodes différentes (chromazurol, ériochrome cyanine et 8-quinolinol). La méthode colorimétrique au chromazurol semble la plus satisfaisante.

Chemische Beständigkeit von Glas: Aluminiumoxidbestimmung in Auslauglösungen

Neun Laboratorien analysierten zwei Modellösungen mit Al_2O_3-Gehalten von 1 und 10 ppm und eine Auslauglösung mit 0,5 ppm Al_2O_3, wobei drei unterschiedliche Verfahren verwendet wurden: Chromazurol, Eriochromcyanin und 8-Hydroxychinolin. Die kolorimetrische Methode mit Chromazurol erwies sich als das am meisten befriedigende Verfahren.

Sub Committee A 2 reports on the determinations of boric oxide [1], silica [2], and calcium and magnesium oxides [3] have already been published. The programme of work to produce methods for the analysis of durability extracts is completed in this issue of "Glastechnische Berichte" by further reports on the determinations of the oxides of sodium and potassium [4], iron [5], and lead [6]. This present report describes the work involved in developing a colorimetric method, using chromazurol, for determining very small amounts of aluminium oxide which might be expected in durability extract solutions. The working details of a recommended procedure are described in 4. Appendix.

1. Determination of aluminium oxide

1.1. General considerations

The amounts of aluminium extracted from most glasses by the methods normally used for glass durability testing are extremely small and so it is necessary that any chemical analysis method used to determine the aluminium must be of trace analysis quality. Because of this fact it was decided that the most widely applicable approach would probably be via a colorimetric method although, compared with many other elements, there is a lack of outstanding reagents for the separation and colorimetric determination of aluminium.

Before this course was decided upon a spectrographic method was considered. It was found that, although it would undoubtedly be an ideal technique, few members had the necessary equipment for a collaborative study, and this requirement of specialist equipment and expertise could limit its use as a standard method. Also, during collaborative study of colorimetric procedures, some determinations were made by atomic absorption spectroscopy and these results appeared to be promising.

Three colorimetric reagents were selected for the collaborative investigation. The choice was not simple because although the number of reagents available is quite considerable, none of them were particularly outstanding. In the event the Committee chose to examine chromazurol [7], eriochrome cyanine [8] and 8-quinolinol [8]. The first two reagents form a strongly coloured "lake", the exact nature of which is often uncertain. They have been thought of as internal complexes of Al in colloidal solution, or as colloidal $Al(OH)_3$ on which the organic compound is absorbed in one form or another. This is a definition of a lake in the strict sense and there is usually a pronounced shade of colour involved when it is formed. The lake formations result in colloidal suspensions of varying stability, and the pH range over which they can exist is approximately that in which $Al(OH)_3$ is capable of existing. For reproducible results, very close control of the pH is necessary, because this affects not only the speed and extent of the lake formation but also the colour of the excess reagent. Various metal ions, especially Fe^{3+} and Cu^{2+}, also form strongly coloured lakes, whilst anions tend to reduce colour. The third reagent, 8-quinolinol, is used to form the hydroxyquinolate of aluminium, which is then extracted into chloroform to form a yellow solution. A good separation from calcium, magnesium, beryllium, manganese, chromium and the rare earth oxides is achieved from a solution having a pH 4.5 to 5.0. However many other metals, including Fe^{3+}, are similarly extracted, and it is necessary to take precautions, such as the use of complexing agents, in order to eliminate these interferences.

1.2. Collaborative work

Having agreed upon the reagents to be used, members were asked to submit analysis methods and from these a detailed procedure using eriochrome cyanine was prepared.

Some difficulties were encountered in the case of the other two reagents probably because of a general lack of previous experience with them. It was eventually agreed that there should be no specific recommendations made but that members should proceed with the determination using the expertise available to them.

In this initial stage of the investigation a project was initiated whereby members were provided with about 100 ml each of the following solutions:

K_2O – 100 ppm in distilled water,

PbO – 100 ppm in 1 : 1 nitric acid,

Fe_2O_3 – 10 ppm in 1 : 1 nitric acid,

Al_2O_3 – 10 ppm in 1 : 1 nitric acid.

From these the 10 ppm solution was to be used with suitable dilutions to construct a calibration graph and then the Al_2O_3 content of a "mixed solution" was to be determined. This "mixed solution" was to be prepared using all four of the distributed solutions and then diluted to produce an Al_2O_3 concentration of about 1 ppm. The results obtained are given in table 1 and show that the within-laboratory reproducibilities for all three reagents are generally good but that the between-laboratory variation could be improved. Whilst the overall mean values obtained with eriochrome cyanine and chromazurol are very close, the coefficient of variation of the former is only about half that of the latter. This may indicate the value of actually specifying a procedure to be followed but even so there was much criticism of both methods. Clearly none of the reagents could be selected as being superior and so further consideration was given to the working details.

In the case of eriochrome cyanine the work of Hill [9] was discussed. This involved the formation of an extremely stable coloured compound of aluminium formed by combining a heterocyclic fatty acid with the aluminium eriochrome cyanine R complex. For 8-quinolinol the paper by Villarreal, Krsul and Barker [10] claimed a highly selective method using the extraction of aluminium with N-benzoyl-N-phenylhydroxylamine (BPHA) into benzene, complexing with 8-quinolinol and then back extraction into chloroform. Again, though, at this stage no specific method using chromazural could be recommended.

In the further collaborative work determinations were made at the 10 ppm Al_2O_3 level because some members had experienced considerable difficulty when measuring at 1 ppm. Table 2 shows the results achieved in this second exercise and it can be seen that there was still need to improve the method. In fact little significant progress appeared to have been made and, since the results still did not show a definite bias towards one particular reagent, it was decided to concentrate further work on the use of chromazurol because this reagent appeared to offer fewer practical complications.

Table 1. Results obtained using a specified eriochrome cyanine method but unspecified chromazurol and 8-quinolinol methods

Laboratory	Concentration of Al_2O_3 in ppm		
	eriochrome cyanine	chromazurol	8-quinolinol
A	0.86 0.86 0.86	–	–
B	0.86	1.18 1.20	–
C	0.90 0.84	–	–
D	–	1.22 1.25 1.27	–
E	–	–	1.1 0.95
F	–	0.79 0.77 0.82	–
G	1.19 1.18	0.96 0.93	–
H	0.98 1.19 1.15 1.10 1.01 1.09	–	–
J	1.15 1.13	–	–
K	0.94 1.06 1.07	–	–
Overall mean	1.03	1.04	–
Range of results	0.84 to 1.19	0.77 to 1.27	–
Standard deviation	± 0.12	± 0.21	–
Coefficient of variation in %	12	21	–

Table 2. Results obtained at a higher, 10 ppm Al_2O_3, level using reconsidered methods

Laboratory	Concentration of Al_2O_3 in ppm		
	eriochrome cyanine	chromazurol	8-quinolinol
A	10.9 10.6 10.0 9.2 10.4 10.0 9.0	–	–
L	8.5 8.8	10.5 10.8	8.6
M	11.5 10.8 10.3 11.6 11.5 10.5 11.0 11.5 11.5	10.0 10.0 9.3 10.1 9.3 10.1 9.4	10.0 10.0 9.0 9.0
N	11.5 11.4 12.0	9.6 9.8	11.1 9.4 9.1
E	8.8 9.8 9.2 11.5	–	10.0 9.7 9.7
F	12.6 10.5 11.4 12.4 11.3 10.8 11.3 12.2	10.8 10.5 11.4 10.7 10.5 10.2 10.7 10.2	11.2 11.3 10.0 11.0
G	11.9 10.2 12.5 9.0 9.4 10.1	9.9 9.9 9.9 10.1	–
H	12.4 11.1	9.7 9.7	9.9 9.6
K	12.0 11.5 10.9	12.0 13.4 11.2	–
Overall mean	10.80	10.36	9.93
Range of results	8.5 to 12.6	9.6 to 13.4	8.6 to 11.3
Standard deviation	± 1.1	± 0.88	± 0.80
Coefficient of variation in %	10.1	8.5	8.1

Table 3. Results obtained using chromazurol method based on the work of Bhargava and Hines [12]

Laboratory	Mean value ppm Al_2O_3	Range of results	Standard deviation
A	9.65	9.2 to 10.4	± 0.42
D	9.34	8.8 to 9.7	± 0.24
E	9.35	9.0 to 9.6	± 0.26
F	10.11	9.9 to 10.3	± 0.12
G	9.95	9.9 to 10.0	± 0.05
H	9.89	8.9 to 11.0	± 0.71
K	9.61	9.2 to 9.9	± 0.29
M	9.88	9.0 to 10.5	± 0.46
P	9.94	9.6 to 10.0	± 0.08
Grand mean	9.74	–	–
Range of means	9.34 to 10.11	–	–
Standard deviation	± 0.27	–	–
Coefficient of variation in %	2.8	–	–

Table 4. Results obtained when the proposed chromazurol method was used on synthetic solutions

Laboratory	Synthetic solution – chromazurol	
	Solution A (ppm)	Solution B (ppm)
G	1.07	10.58
L	1.11	9.90
P	1.00	9.80
Q	0.98	9.94
H	0.83	7.66
Mean	1.00	9.49
Range of results	0.83 to 1.11	7.66 to 10.58
s	0.12	1.27
Coefficient of variation in %	12.0	12.4
	Synthetic solutions – atomic absorption	
G	Estimated ratio of solution A to solution B as 21 : 211 digits.	
H	Solution A too dilute to analyse. Solution B about 7 to 9 ppm.	

A procedure using chromazurol and based upon the work of Thierig [11] was discussed but it was agreed that it would be too comprehensive for analysing glass durability solutions, because precautions were included against many interfering elements which would never be present in such solutions. It was therefore decided that a more simplified chromazurol method, based upon the work of Bhargava and Hines [12] should be used, and new solutions were prepared in a similar manner to those previously. The results of this exercise are shown in table 3, where it can be seen that the between laboratory reproducibility, shown by the standard deviation and the coefficient of variation are improvements over the corresponding values shown in table 2.

Table 5. Results obtained when proposed chromazurol method was applied to an extract solution from a soda-lime-silica glass

Laboratory	Al_2O_3 in ppm	Remarks
A	0.59	10 results range 0.50 to 0.68
G	0.24	
L	0.45	
P	0.51	
D	0.28	2 results range 0.27 to 0.28
E	0.50	
Q	0.57	
H	0.46	5 results range 0.37 to 0.59
K	0.38	
Mean	0.43	
Range of results	0.24 to 0.59	
s	0.12	
Coefficient of variation in %	27.9	
	Durability extract – atomic absorption	
N	0.60	3 results range 0.52 to 0.68

In an attempt to clarify the position further it was agreed that alumina determinations by the chromazurol method should be made using an actual durability extract solution produced by autoclaving a soda-lime-silica glass for 1 hour at 121 °C as described in the European Pharmacopoeia. In addition, since there were already two synthetic solutions containing known amounts of CaO, MgO, Na_2O, K_2O and Al_2O_3 in circulation for collaborative work on CaO and MgO determinations, it was agreed that these solutions should also be analysed for Al_2O_3 by chromazurol and, if facilities allowed, by atomic absorption spectroscopy.

The results on the synthetic solutions are given in table 4 and when compared with those shown in tables 1 and 2 they suggest that, at the lower level of concentration, the experience gained with the procedure has produced an improvement in the reproducibility. At the higher, 10 ppm, level, though, such is not the case and an even greater variability has resulted.

The results obtained using actual durability extract solutions, shown in table 5, indicate that the probable level of the aluminium concentration is even lower than that anticipated by the lowest standard solution. This being so it may well be that a standard deviation of ± 0.1, even though the coefficient of variation is quite high, could be considered to be satisfactory.

Clearly there were too few determinations made by atomic absorption spectroscopy to permit an assessment of this technique.

2. Conclusions

On consideration of the collaborative work to date, the colorimetric chromazurol method appears to be the most satisfactory from an operational point of view and,

at the low concentrations of Al_2O_3 expected in durability extract solutions, is probably as accurate as any other generally available method. Some success may possibly be expected in the future using an atomic absorption method if the solution to be atomized is concentrated to contain about 5 ppm Al_2O_3.

3. References

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4. Appendix. Determination of aluminium oxide in durability extract solutions

4.1. Principle

The colour of the aluminium/chromazurol complex is developed and the optical density measured at 545 nm using 10 mm cells.

4.2. Reagents

Distilled or de-ionised water and analytical grade reagents must be used throughout.

Acetate buffer solution: Dissolve 75 g of sodium acetate trihydrate, $CH_3CO_2Na \cdot 3H_2O$, in water and dilute to 1 litre. Store in a plastic bottle.

Ascorbic acid: 1.6% w/v. Prepare a fresh solution immediately before use.

Chromazurol S: Dissolve 0.10 g of the solid in 50% w/v ethanol and dilute to 250 ml with 50% w/v ethanol.

Hydrochloric acid: 2 N.

4.3. Standard solutions

Aluminium stock solution: 0.01 M in 0.1 N HCl. Dissolve 2.414 g of aluminium chloride hexahydrate, $AlCl_3 \cdot 6H_2O$ in water to which is added 50 ml of 2 N HCl. Transfer the solution to a 1 litre volumetric flask, dilute to the mark and mix thoroughly.

1 ml $\equiv$ 510 µg Al_2O_3.

Aluminium working solution I: Pipette 10.0 ml of the aluminium stock solution into a 1 litre volumetric flask, add 50 ml of 2 N HCl, dilute to the mark and mix thoroughly.

1 ml $\equiv$ 5.10 µg Al_2O_3.

Aluminium working solution II: Pipette 100.0 ml of aluminium working solution I into a 1 litre volumetric flask, add 45 ml of 2 N HCl, dilute to the mark and mix thoroughly.

1 ml $\equiv$ 0.51 µg Al_2O_3.

4.4. Calibration graph

Transfer accurately measured aliquots of aluminium working solutions I or II to separate 100 ml volumetric flasks to cover the range 0 to 25 µg Al_2O_3. Dilute, where necessary, to about 5 ml, then add 10 ml of ascorbic acid solution, mix thoroughly and allow to stand for 10 minutes. Add 30 ml of acetate buffer and 5 ml of chromazurol S solution, dilute to the mark, mix thoroughly and allow to stand again for 10 minutes.

Measure the optical densities of the solutions containing aluminium, using the solution containing no added aluminium as the blank, at 545 nm in 10 mm cells and plot the graph of µg Al_2O_3 versus optical density.

4.5. Procedure

Transfer a suitable aliquot of the extract solution, or concentrate the extract to a suitable volume and transfer to a 100 ml volumetric flask. Add 10 ml of ascorbic acid solution and proceed as described in section 4.4. above.

Measure the optical density at 545 nm using 10 mm cells against a blank solution prepared from the same volumes of reagents used in the durability test, but which have not been subjected to the heating cycle.

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