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The chemical durability of glass: determination of lead in extract solutions

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

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Nine laboratories analysed a simulated durability extract solution containing about 10 ppm PbO using either a dithizone colorimetric method or an atomic absorption procedure. Fourteen laboratories then analysed actual durability extract solutions from lead glass containing 6, 10, 24, and 30% PbO respectively, and demonstrated that both analytical procedures are satisfactory for the determination.

La durabilité chimique du verre: dosage du plomb dans les solutions

Neuf laboratoires ont analysé deux solutions de synthèse de même composition que celle d'un essai de durabilité, contenant environ 10 ppm de PbO, par une méthode colorimétrique au dithizone et à l'aide d'un procédé par absorption atomique. Quatorze laboratoires ont ensuite analysé des solutions réelles de verres au plomb contenant respectivement 6, 10, 24, et 30% de PbO, pour démontrer que les deux méthodes d'analyse permettaient d'obtenir des résultats satisfaisants.

Chemische Beständigkeit von Glas: Bleibestimmung in Auslauglösungen

Neun Laboratorien führten Analysen einer Modellösung mit 10 ppm PbO unter Verwendung eines kolorimetrischen Dithizonverfahrens oder der Atomabsorption durch. Ferner analysierten 14 Laboratorien Auslauglösungen von Bleiglasproben mit PbO-Gehalten von 6, 10, 24 bzw. 30%. Es wurde bewiesen, daß beide Analysenverfahren für die Bleibestimmung geeignet sind.

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 aluminium [4], sodium and potassium [5], and iron [6].

Traditionally, when referring to glass compositions, the metals are expressed as their oxides, usually the highest stable oxide, and this custom has been followed in all of these reports, even though, in extract solutions the metals will be present, primarily, in ionic form. Traditionally, also, the chemical resistance of a glass has been indicated by the volume of acid required to neutralize the extract solution or by the total alkalies determined in such solutions. The methods of analysis described in this series of reports enable an almost complete analysis of a durability extract solution to be made and such information can be far more useful than the limited analyses previously available.

The members of the Sub Committee during the work on lead determinations suggested in their preliminary considerations that a colorimetric procedure, using dithizone, and an atomic absorption spectrophotometric technique should be examined. A collaborative investigation applying both procedures to a simulated extract solution and then to actual extract solutions was then made and the working details of the eventually agreed methods are given in 5. Appendix.

1. Discussion

Sandell [7] proposed a dithizone colorimetric method for lead determination which depends on the extraction of the red-coloured Pb-dithizone complex into chloroform at pH 11.5. The measurement is made in ammoniacal sulphite-cyanide solution and under these conditions the effects of certain interferring elements are marked. A dithizone colorimetric method has also been used by El-Shamy and Taki-Eldin [8] in a study of the chemical durability of lead silicate glasses. It has been shown that the Pb-dithizone complex is slowly decomposed in solutions of pH greater than 10.5 and the type and concentrations of anions present can also influence the result. Therefore, the procedure described in 5. Appendix should be followed precisely.

In the published literature concerning the determination of lead by atomic absorption interferences by common ions have not been observed. It seemed, therefore, that the determination of lead could be carried out using the solutions acidified with nitric acid and with an air-acetylene flame. The optimum working range appeared to be 4 to 40 ppm PbO and the suitable wavelength to be 217 nm. For lower concentrations of lead oxide solvent extraction with ammonium pyrrolidine dithiocarbamate and methylisobutylketone has been recommended [9]. The AAS technique for determining lead oxide has been used recently by Pohlmann [10] for studying the corrosion of lead-silicate glasses.

2. Experimental work

Preliminary experiments using the dithizone and atomic absorption methods were made on synthetic lead oxide solutions produced by mixing one volume of each solution containing (a) 10 µg Fe_2O_3, (b) 102 µg K_2O, (c) 102 µg PbO and (d) 9.45 µg Al_2O_3 and diluting to 10 volumes. The PbO content in the solution was then determined by the procedures described in 5. Appendix and the results obtained are given in table 1.

A statistical examination of the results showed that the value of 11.4, obtained by Lab. A by the dithizone method, was outside the range of mean value ± 2 SD. When the mean value and standard deviations were recalculated omitting this value the results show that both methods are equal in precision and are satisfactory at these levels of PbO concentrations. Observation made by the members suggested that although the dithizone method was more sensitive than atomic absorption it needed more delicate control. One of the members had difficulties in producing a linear calibration graph and had to use the so called "spread technique" using standard solutions of lower and higher concentration than the solution analysed. There were no problems when atomic absorption spectroscopy was used.

Palecek then prepared durability extract solutions from samples of four lead crystal glasses containing respectively 6, 10, 24, and 30% by weight of lead oxide (PbO), using the autoclave procedure described in the European Pharmacopoeia. A sufficient number of samples of each type of glass were used to produce about 2 litres of extract solution. Each of the four solutions was acidified to about 0.001 N with nitric acid and portions of each were distributed, in plastic bottles, to each member of the Sub Committee. Members were asked to analyse the solutions for lead content using either or both the dithizone colorimetric or the atomic absorption techniques, described in 5. Appendix and the results obtained are shown in table 2.

It is clear that the actual level of lead present in these solutions is only about 10% of that included in the synthesised solutions. Even so, the agreement between laboratories and between methods appears to be satisfactory as shown by the standard deviation and mean values, respectively.

The mean values of the results obtained by the dithizone colorimetric method may be slightly higher than those obtained by atomic absorption, but this difference may be influenced by the "higher" values obtained by Lab. 9. At these levels of concentration, though, the difference is thought not to be analytically significant.

3. Observations

It is appreciated that high temperature durability tests are rarely, if ever, made on lead crystal glasses because articles made from such glasses are not normally used at such temperatures. Even so lead crystal glasses may be required to comply with certain proposed international regulations which include such a test and which are currently under discussion. The results obtained in this investigation show that the amounts of lead released into the test liquid can be determined satisfactorily by both of the methods described in 5. Appendix.

Table 1. Results obtained for the determination of lead in a synthetic durability extract solution

Laboratory	ppm PbO found by					
	Dithizone			AAS		
A	11.4			10.3		
B	10.5	10.4		10.3	10.3	
F	10.2	10.2	10.2	10.7	10.6	10.0
	10.2	10.1		10.7	9.8	9.8
I	–			10.5	10.4	
J	–			10.3	10.4	
K	10.6	10.1	10.8	–		
	10.0	10.6	10.7			
L	–			10.0		
M	–			10.5	10.5	10.3
N	10.0	9.9	10.7	–		
	10.6	10.5	10.8			
	10.9	10.3				
Overall mean	10.4			10.3		
Standard deviation	0.37			0.28		
Re-calculated values omitting Lab. A, Dithizone result						
Overall mean	10.4			–		
Standard deviation	0.30			–		

Table 2. Results obtained for the determination of lead in actual durability extract solutions

Laboratory	ppm PbO found from glass containing							
	6% PbO		10% PbO		24% PbO		30% PbO	
	Col.	AAS	Col.	AAS	Col.	AAS	Col.	AAS
A	–	1.1	–	1.1	–	1.2	–	1.6
B	1.1	1.1	1.1	1.0	1.2	1.2	1.6	1.6
C	–	1.2	–	1.3	–	1.2	–	1.3
D	–	1.2	–	1.2	–	1.3	–	1.6
E	–	1.1	–	1.1	–	1.2	–	1.6
F	1.1	1.1	1.1	1.1	1.2	1.2	1.6	1.6
G	1.3	–	1.2	–	1.5	–	1.9	–
H	–	1.1	–	1.1	–	1.3	–	1.5
I	–	1.5	–	1.4	–	1.5	–	1.3
J	1.3	1.1	1.4	1.0	1.3	1.3	1.7	1.5
K	–	1.1	–	1.1	–	1.3	–	1.6
L	–	1.1	–	1.0	–	1.1	–	1.5
M	–	1.0	–	1.0	–	1.1	–	1.5
O	–	–	–	1.0	–	1.1	–	1.5
Mean	1.20	1.14	1.20	1.11	1.30	1.23	1.70	1.52
Standard deviation	0.11	0.12	0.14	0.13	0.14	0.11	0.14	0.13

4. References

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5. Appendix. Determination of lead oxide in extract solutions

5.1. Dithizone method

5.1.1. Principle

Lead ions produces a red coloured complex with dithizone (1:5 diphenylthiocarbazone) in solution at pH 11.5 and this complex is extractable with chloroform. The optical density of the organic phase is measured at 520 nm and Lambert-Beer's law is obeyed in the range of 4 to 40 µg PbO.

5.1.2. Reagents

All reagents must be of the "low lead" grade and precautions must be taken throughout the determination to avoid contamination of solutions. High-purity water must be used throughout.

Ammonium hydroxide: d = 0.880 and 5 M.

Chloroform: Transfer 250 ml of chloroform to a 500 ml separating funnel, add 25 ml of water containing 1 ml potassium cyanide solution and add about 20 drops of ammonium hydroxide (d = 0.880). Shake thoroughly for 1 minute and allow to settle. Reject the aqueous layer, wash the chloroform again with water, then filter into a clean, dry bottle.

Dithizone: 1:5 diphenylthiocarbazone
$(C_6H_5N:NCS\ NH\ NHC_6\ H_5)$.

High purity water: The water used in this determination should have a conductivity, measured in an in-line cell at 25 °C immediately prior to use of not greater than 0.15 µmho[1]) per cm. It should be free from lead, when measured by AAS or by dithizone and may be prepared either by passing distilled water through a bed of mixed, nucleus grade, ion-exchange resin and then through a cellulose outer membrane filter having openings not exceeding 0.45 µm or by re-distilling once-distilled or deionised water from a chemically resistant, borosilicate glass still.

Hydrofluoric acid: 40% w/w.

Lead nitrate.

Nitric acid: d = 1.42 and 1 + 99.

Potassium cyanide solution: 10% w/v.

Sodium sulphite solution: 2% w/v.

Ammoniacal sulphite/cyanide solution: Mix 340 ml of ammonium hydroxide (d = 0.880), 75 ml of sodium sulphite solution, 30 ml of potassium cyanide solution and 605 ml of water in a 2 l flat-bottom flask, stopper and store (N.B. The concentrations of these reagents are critical).

Dithizone stock solution 0.1% w/v in chloroform: filtered and stored in refrigerator.

Dithizone working solution: Transfer 6 ml of the stock solution, 9 ml of water and 1 ml of ammonium hydroxide (5 M) to a separating funnel and mix thoroughly. Allow to settle, then reject the chloroform layer and centrifuge the aqueous layer until clear. Prepare this solution freshly immediately before use.

Standard lead solution: Dissolve 1.484 g of lead nitrate in water, add 10 ml of nitric acid (d = 1.42) and dilute to the mark in a 1 litre volumetric flask.

1 ml ≡ 1 mg PbO.

Dilute standard lead solution: Immediately before use dilute 1 volume of the standard lead solution to 100 volumes with water.

1 ml ≡ 10 µg PbO.

5.1.3. Procedure

This procedure must be followed precisely. Transfer the whole, or an aliquot, of the durability extract solution to a platinum dish of suitable size and evaporate to dryness. Add 0.5 ml of hydrofluoric acid and 1 ml of nitric acid (d = 1.42) to the dish, swirl to dissolve the residue and again evaporate to dryness. Dissolve the residue in 5 ml of nitric acid (1 + 99) and transfer to a 100 ml separating funnel, restricting the total volume to 10 ml.

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[1]) µmho ≙ µS.

Add 30 ml of ammoniacal sulphite/cyanide solution, 10 ml of chloroform and 0.5 ml of dithizone working solution. Shake the solution vigorously for 1 minute and allow to settle. Allow the chloroform layer to run into a filter tube, porosity grade 1 with a 3 cm layer of treated cotton wool or phase separating paper, and collect the filtrate in a 15 ml volumetric flask. Shake the aqueous layer with the further 3 ml of chloroform, allow to settle again, collect the chloroform layer, via the same filter tube, in the 15 ml flask. Add chloroform to the flask, dropwise and through the filter tube, until the solution is diluted to the mark. Mix the solution thoroughly and measure the optical density at 520 nm using 40 mm cells.

5.1.4. Calibration

Transfer 0.0; 1.0; 2.0; 3.0 and 4.0 ml aliquots of the dilute standard lead solution into separate 100 ml separating funnels, dilute each to 10 ml with nitric acid (1 + 99) and proceed as from "Add 30 ml of ammoniacal sulphite/cyanide solution" in section 5.1.3.

Plot the graph of optical density against µg PbO.

5.1.5. Blank determination

Determine the blank value of the reagents by following the procedure described in section 5.1.3. but using high purity water instead of the sample solution.

5.2. Atomic absorption spectroscopy

5.2.1. Principle

The solution to be analysed is aspirated into the air-acetylene flame and the absorption at a wavelength of 217 nm is measured.

5.2.2. Reagents

Nitric acid: d = 1.42.

Standard lead solution: Dissolve 1.484 g of lead nitrate in water, add 10 ml of nitric acid (d = 1.42) and dilute to the mark in a 1 litre volumetric flask.

1 ml ≡ 1 mg PbO.

Dilute standard lead solution: Immediately before use dilute 1 volume of the standard lead solution to 100 volumes with water.

1 ml ≡ 10 µg PbO.

5.2.3. Procedure

Transfer the whole, or an aliquot, of the extract solution to a suitable volumetric flask to give the lead concentration in the range 10 to 30 ppm; add 1% of the flask volume of nitric acid (d = 1.42), dilute to the mark with water and mix thoroughly. Determine the lead concentration of the sample solution by atomic absorption spectrophotometry by reference to a calibration graph or by using the "spread technique" with lead solutions containing lower and higher concentration of lead oxide than the sample solution.

5.2.4. Calibration

For the calibration use 0; 1.0; 2.0; 3.0 and 4.0 ml of dilute standard lead solution in the suitable volumetric flasks of the same volume as in the case of solution analysed, add 1% of the flask volume of nitric acid (d = 1.42), dilute to the mark with water, mix thoroughly and measure. Either plot the absorption against concentration of PbO or use two standard solutions with lower and higher concentration of PbO.

5.2.5. Blank determination

Prepare a blank solution as described in section 5.2.3., but using high purity water instead of the extract solution.

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