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

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

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Nine laboratories accurately determined Fe_2O_3 in a simulated durability extract solution containing 1.0 ppm Fe_2O_3, 0.95 ppm Al_2O_3, 10.2 ppm K_2O, and 10.2 ppm PbO by extraction with chloroform and colorimetric determination with bathophenanthroline. The method has greater sensitivity and probably greater freedom from interferences than the experiments demonstrate. Accurate results in single laboratories were also obtained by a variant bathophenanthroline procedure, an orthophenanthroline procedure and atomic absorption spectroscopy using an air-acetylene flame.

La durabilité chimique du verre: dosage du fer dans les solutions.

Neuf laboratoires ont fait un dosage précis de Fe_2O_3 dans une solution de synthèse de même composition que celle d'un essai de durabilité, contenant 1,0 ppm de Fe_2O_3; 0,95 ppm de Al_2O_3; 10,2 ppm de K_2O et 10,2 ppm de PbO, par extraction au chloroforme et détermination colorimétrique à la bathophénantroline. Les essais n'ont pas permis de mettre en évidence toute la sensibilité de cette méthode et de prouver à quel point elle permet d'éviter les interférences. Certains laboratoires ont obtenu des résultats précis à l'aide des méthodes suivantes: une variante du procédé à la bathophénantroline, un procédé à l'orthophénantroline, un procédé de spectrographie par absorption atomique avec utilisation d'une flamme d'air et acétylène.

Chemische Beständigkeit von Glas: Eisenbestimmung in Auslauglösungen

In einer Modellösung der Zusammensetzung (Angaben in ppm) 1,0 Fe_2O_3; 0,95 Al_2O_3; 10,2 K_2O und 10,2 PbO wurde von neun Laboratorien Fe_2O_3 durch Extraktion mit Chloroform und kolorimetrisch mit Bathophenanthrolin bestimmt. Die Methode ist empfindlicher und weniger störungsanfällig als es die Versuche zeigen. In einzelnen Laboratorien wurden auch genaue Ergebnisse mit Orthophenanthrolin und Atomabsorptionsspektroskopie (Luft-Acetylenflamme) erhalten.

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 lead [6]. In these documents the metals are reported as the corresponding oxides which is customary when referring to glass compositions, although in the extract solutions they are present, primarily, in ionic form. The determination of individual elements in an extract can provide insights that are useful for some purposes beyond those afforded by the usual determination of total solids or total alkaline material.

The members of the Sub Committee suggested in their preliminary considerations colorimetry using bathophenanthroline [7] or orthophenanthroline, atomic absorption spectroscopy and emission spectroscopy as possible methods for the determination of iron. From their considerations the Sub Committee undertook a cooperative study using the bathophenanthroline colorimetric procedure and from this the proposed method of analysis, working details of which are given in 3. Appendix I, has resulted.

1. Discussion

Smith, McCurdy and Diehl [7] state that a long list of ions including chloride, sulphate, nitrate, acetate, perchlorate, lithium, sodium, potassium, calcium, magnesium, barium, cerium, chromium, boron, aluminium, lead, arsenic, copper, titanium, and manganese do not interfere in the determination of iron with the bathophenanthroline-extraction procedure and their successful application of the general procedure to raw, treated, and sea water indicate that moderate amounts of silica do not interfere. Cluley and Newman [8] describe a procedure similar in many details to that of 3. Appendix I and affirm the general absence of interferences. Tetlow and Wilson [9], who used reduction by hydroxylammonium chloride and extraction with isopentanol, demonstrated the absence of interference from 10 ppm of "silicate", 10 ppm of calcium, 10 ppm magnesium and 10 ppm of "orthophosphate" simultaneously present on the determination of 0.025 ppm of iron.

It appears that the method is applicable to extract solutions obtained from a much wider variety of glasses than the present experiment suffices to demonstrate. The procedure given in 3. Appendix I will detect 0.01 ppm Fe_2O_3 and it can be readily modified to enhance the sensitivity. Bacon, Russell, Baumgartner et al. [10] used such a procedure to measure the iron extracted by water and/or 3% acetic acid solution from 300 to 350-ml beverage bottles in 60 minutes at 121 °C. The glasses contained 0.052 to 0.23% Fe_2O_3 (total iron). The concentration of iron in the extracts ranged from 0.002 to 0.024 ppm Fe_2O_3 and amounted to 0.02 to 0.39% of the total extracted solids.

Table 1. Determination of Fe_2O_3 in simulated extract solution

Laboratory	ppm Fe_2O_3 found by					
	bathophenanthroline			orthophen-anthroline		AAS
A	1.0	1.0				
B	0.98	0.98	1.00			
C	1.10	1.16				
D	0.98	0.98				
E	1.07	1.04	1.04[1])			1.00
F	1.01	1.00	1.01			
	1.01					
G	1.00	0.98		0.99	0.99	
H	0.95	0.95	0.96			
	0.95	0.93	0.92			
J	1.14	1.08	0.94			
	1.04	1.05	1.04			
K	1.02					
Overall mean	1.01					
Range of results	0.92 to 1.16					
Standard deviation	± 0.05					

[1]) This laboratory extracted the color complex with hexanol instead of chloroform essentially following the procedure of Smith, McCurdy and Diehl [7].

Table 2. Results for the determination of Fe_2O_3 by AAS in simulated durability extract solutions

Solution	Fe_2O_3 added in µg/ml	Fe_2O_3 found in µg/ml		
1	0	0.02		0.01
2	0.1	0.10	0.10	0.12
3	0	0.00		0.03
4	0.5	0.49	0.51	–

As an example of adaptation of this principle to a higher sensitivity, Bacon et al. [10], transferred 250 ml of aqueous (water or 3% acetic acid) extract solution into a separating funnel and reduced with hydroxylammonium chloride. Bathophenanthroline was added, the pH adjusted to 4.5 to 5.0 and the bathophenanthroline-ferrous ion complex extracted with 20 ml of n-hexanol. The optical density of the hexanol solution was measured at 533 nm in 50 mm cells.

In determining trace amounts it may be necessary to purify some of the reagents by extraction with bathophenanthroline in order to keep the blank low relative to the concentrations being determined.

Table 1 shows that all co-operators obtained concordant results. In Nordberg's laboratory the atomic absorption determination was made using an air-acetylene flame with the nitric acid content of standards and simulated extract carefully matched. No one reported difficulty with the recommended procedure but several pointed out the need for immaculate technique in working at low levels of concentration.

In a later collaboration to investigate some possible interferences in the determinations of soda and potash Mayaux prepared and distributed solutions containing the following:

Solution 1: between 8 and 10 µg Na_2O/ml,
0 µg Fe_2O_3/ml;
Solution 2: between 8 and 10 µg Na_2O/ml,
1 µg K_2O/ml,
10 µg CaO/ml,
5 µg MgO/ml,
1 µg Al_2O_3/ml,
0.1 µg Fe_2O_3/ml;
Solution 3: between 0.4 and 0.6 µg Na_2O/ml,
0 µg Fe_2O_3/ml;
Solution 4: between 0.4 and 0.6 µg Na_2O/ml,
0.5 µg K_2O/ml,
25 µg CaO/ml,
0.5 µg MgO/ml,
15 µg Al_2O_3/ml,
0.5 µg Fe_2O_3/ml.

A full report on this work will be issued in due course but Bouligaud, Nordberg and Linzander took advantage of the opportunity to measure the iron contents of those solutions by atomic absorption spectroscopy. All used an air/acetylene flame and their results are shown in table 2.

The Sub Committee did not proceed with a complete collaborative investigation of this method for measuring small concentrations of iron because it was considered that the bathophenanthroline colorimetric procedure was sufficiently sensitive and more widely applicable. However, the results do indicate that the AAS technique could be equally suitable and a description of the procedure adopted by Bouligaud is given in 4. Appendix II, for information.

2. References

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3. Appendix I. Determination of ferric oxide in extract solutions

3.1. Principle

Ascorbic acid is added to reduce iron to the ferrous state. Bathophenanthroline (4 : 7-diphenyl-1 : 10-phenanthroline) is added, the solution is buffered between pH 4 and 6, and the resulting tris (4 : 7-diphenyl-1 : 10-phenanthroline)-ferrous iron complex is extracted into chloroform. The optical density of the solution is measured at 533 nm using 40 mm cells.

3.2. Reagents

Analytical grade reagents must be used throughout.

Ammonium hydroxide solution: approximately 5 N.

Ammonium ferrous sulfate: $(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O$.

Ascorbic acid: 10% w/v, freshly prepared.

Bathophenanthroline (0.001 M): Dissolve 0.0332 g of 4 : 7-diphenyl-1 : 10-phenanthroline in 100 ml of ethanol.

Chloroform.

Ethanol: absolute.

Hydrochloric acid: d = 1.18.

Perchloric acid: 60% w/v.

Sodium acetate, trihydrate: $CH_3COONa \cdot 3H_2O$.

3.3. Standard solutions

3.3.1. Standard iron solution

Dissolve 0.4911 g of ammonium ferrous sulphate in water and add 10 ml of hydrochloric acid. Transfer to a 1 litre volumetric flask, dilute to the mark and mix thoroughly.

1 ml = 0.1 mg Fe_2O_3 (100 μg).

3.3.2. Dilute standard iron solution

Pipette 10 ml of the standard iron solution into a 1 litre volumetric flask, dilute to the mark and mix thoroughly. This solution must be freshly prepared.

1 ml = 1.0 μg Fe_2O_3.

3.4. Procedure

Determine the blank value concurrently with the sample value by following the procedure exactly but using distilled water instead of the extract solution.

Transfer a measured volume of extract solution to a 100 ml conical flask, dilute if necessary to about 25 ml and add 2.5 ml of perchloric acid. Add 5 ml of ascorbic acid solution, 10 ml of bathophenanthroline, 0.5 g of sodium acetate and mix thoroughly. Adjust the pH to between 4 and 6 by addition of ammonium hydroxide as necessary, using a glass electrode, cover the flask and allow to stand for 20 minutes.

Transfer the solution to a 150 ml separating funnel, add 5 ml of chloroform and shake the mixture vigorously for 30 seconds. Allow the layers to separate, then run the chloroform layer through a glass wool plug in a small filter funnel into a 25 ml volumetric flask. Extract the solution again with a further 5 ml of chloroform and collect the chloroform layer in the same 25 ml volumetric flask. Dilute the combined solutions to the mark with ethanol, mix thoroughly and measure the optical density of the sample solution at 533 nm using 40 mm cells against the blank solution.

3.5. Calibration graph

Pipette aliquots of the diluted standard iron solution, to cover the range 0 to 20 μg Fe_2O_3, into separate 100 ml conical flasks, dilute each to about 25 ml and proceed as described in section 3.4. Plot the calibration graph of optical density against weight of Fe_2O_3.

3.6. Results

Subtract the blank value from the sample value and calculate the concentration of ferric oxide (Fe_2O_3) in the extract solution.

4. Appendix II. Method for the determination of ferric oxide (Fe_2O_3) in durability extract solutions by atomic absorption spectroscopy

4.1. Principle

In the determination of iron by atomic absorption spectroscopy the sample solution is atomized into the flame of an air/acetylene burner and the absorption at the wavelength 248.3 nm is measured.

4.2. Reagents

Analytical grade reagents must be used throughout.

Hydrofluoric acid: 40% w/v (d = 1.14).

Perchloric acid: 65% w/v (d = 1.61).

Hydrochloric acid: 36% w/v (d = 1.19) and 1 + 9.
Ammonium ferrous sulfate: $(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O$.

4.3. Standard solutions

4.3.1. Concentrated ferric oxide solution

Dissolve 4.911 g of ammonium ferrous sulphate in water and add 10 ml of hydrochloric acid (d = 1.19). Transfer to a 1 litre volumetric flask, dilute to the mark and mix thoroughly.

1 ml ≡ 1 mg Fe_2O_3.

4.3.2. Dilute ferric oxide solution

Transfer a 10.00 ml aliquot of the concentrated ferric oxide solution to a 1 litre volumetric flask, dilute to the mark and mix thoroughly. This solution must be freshly prepared.

1 ml ≡ 10 μg Fe_2O_3.

4.3.3. Reference ferric oxide solutions

Pipette 0; 1.00; 2.00; 5.00 and 10.00 ml aliquots of the diluted ferric oxide solution into separate 100 ml volumetric flasks. Add 5.0 ml of hydrochloric acid (1 + 9) to each flask. Dilute to the mark and mix thoroughly.

1 ml ≡ 0; 0.1; 0.2; 0.5; 1.0 μg Fe_2O_3 respectively.

Note: All of the reference solution, the sample solution and the blank must be of the same acidity, 0.5% in hydrochloric acid (d = 1.19).

4.4. Preparation of a calibration graph

The reference solutions are successively atomized into the flame of an air/acetylene burner and the corresponding absorptions noted. Several measurements are made for each solution, the mean values of the readings calculated and used to prepare the calibration graph of absorption versus Fe_2O_3 concentrations.

4.5. Determination of the ferric oxide concentration of the extract solution

Determine the blank value concurrently with the sample value by following the method exactly but using distilled water instead of the extract solution.

Pipette an aliquot of the durability extract solution, containing not more than 25 μg of Fe_2O_3, into a platinum dish; add two drops of hydrofluoric acid and one drop of perchloric acid and evaporate just to dryness.

Add to the residue 1.25 ml of hydrochloric acid (1 + 9) and digest thoroughly with 10 ml of hot water. When solution is complete and cool, transfer to a 25 ml volumetric flask, dilute to the mark and mix thoroughly.

Determine the ferric oxide concentration of the solution as described in section 4.4., then, using the calibration graph, subtract the blank value from the sample value and calculate the Fe_2O_3 content of the sample solution.

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