

New Approach for the Determination of Fluorine in Glass

Nijhuma Kayal^a and Nahar Singh^b

^a Analytical Chemistry Section, Central Glass and Ceramic Research Institute, 196, Raja S.C. Mullick Road, Kolkata-32, India

^b Analytical Chemistry section, National Physical laboratory, Dr K.S. Krishnan Marg, New Delhi-12;

Abstract

The properties of glass critically depend on glass composition. Apart from silica, calcium and aluminium; fluorine is also an essential constituent of the glass, since it enhances several properties of glass. In view of the increasing use of fluorine in glasses, it is necessary to have a rapid, accurate and cost effective method for the determination of fluorine in glass. Keeping the above facts a simple and rapid method has been developed for the quantitative estimation of fluorine in glass materials. The method proposed is based on extraction of fluorine from the glass sample by decomposing the glass sample with fusion mixture of sodium carbonate and zinc oxide. The fluorine is extracted with distilled water and is determined by using lanthanum chloride as titrant. The accuracy of the method has been established by analyzing five replicates of Standard Reference Material of NBS 91 and four different glass samples. The standard deviation has been calculated by analyzing five replicates of each glass sample and reference material by the method proposed. The method proposed is reproducible and the standard deviation in the determination of five replicates is found to <1.3%.

Key words: Fluorine, Glass, Decomposition, Lanthanum chloride

1. Introduction

Literature survey indicate that a number of methods have been reported for the determination of the fluorine in various inorganic materials. Most of the method is based on extraction of fluorine by using Willard and Winter distillation [1-4], Pyrohydrolysis [5-6] and ion exchanger technique [7]. Apart from these methods, measurements of fluorine are also carried out by using ion-selective electrodes [8-10] and it has been established that same results can be achieved with or without distillation. The procedures based on distillation techniques are complex and lengthy but one advantage is that it separates fluorine from those elements, which may interfere. In other instances measurement of fluorine is carried out directly from sample solution obtained by alkali fusion [11-13]. In fusion method either by alkali or by sodium

carbonate there is loss of fluorine due to high temperature, moreover in both techniques there is probability of interference of aluminum, because it forms complex with fluorine. In general major to minor constituents in glass are SiO_2 , Al_2O_3 , PbO , TiO_2 , MgO , B_2O_3 , F , and ZrO_2 while the trace elements like Co , Ni , Fe , Mn and Cr are sometimes found, depends upon the application [14]. Colorimetric methods [15-16] for the determination of fluorine are usually based on mixed-ligand complex formation using La(III) - or Ce(III) - F - Alizarin complexone. These indicators are sensitive, but all are susceptible to interference from Al(III) and Fe(III) . The visual colourimetric method is involved with more uncertainty as the analyst need to be expert in distinguish the colour change of the indicator and need number of sets for comparison. Therefore, it is required to develop sensitive determination and separation methods of fluoride ion without interference from Al(III) and Fe(III) . In earlier study lanthanum [17] was used as titrant for the determination of fluoride ion by titrimetric method in high purity salts, here we have modified the titrimetric method and successfully applied in glass and allied materials. The procedure is based on the fusion of glass sample by sodium carbonate and zinc oxide at 900°C and the fluorine is extracted by hot water. The elements like aluminium, iron and silica, which form complexes with fluorine, retained as insoluble matter in the solution. The trace of soluble aluminum left in filtrate is masked by sulphosalicylic acid and hexamine solution. The liberated fluorine gets complexed by excess lanthanum chloride. The excess lanthanum is determined by back titration with EDTA. The fluorine concentration is calculated on the basis of consumed lanthanum. Four different glass samples have been analyzed using the method proposed and existing method [4] and the results obtained are in good agreement.

2. Experimental

2.1 Reagents and apparatus

Analytical reagent grade chemicals and doubly-distilled water were used throughout for the preparation of solutions and reagents. Glass samples were collected from the glass laboratory of CG& CRI, Kolkata. Calibrated pipettes and volumetric flasks supplied by Borosil Glass Works Ltd. India were used. A platinum crucible of 99.99% purity obtained from Arora Matthey (Kolkata) India, (associate of Johanson Matthey U.K.) was used after cleaning with potassium hydrogen sulphate (KHSO_4) fusion and subsequent washing with de-ionized water before each experiment. UV-VIS spectrophotometer (Perkin Elmer) was used for colourimetric determination. The digestion process was carried out on a Laminar flow bench equipped with an appropriate ventilation system.

2.1.1 Standard sodium fluoride solution:

1000 mg L⁻¹ stock solution of sodium fluoride solution was prepared by dissolving 1.105 g of high purity primary standard grade NaF and it was diluted to 500 mL by de-ionized water. The diluted solutions were prepared by appropriate dilution of the stock solution.

2.1.2 Lanthanum chloride solution:

1000 mg L⁻¹ stock solution of lanthanum chloride was prepared by dissolving 2.6737 g of LaCl₃ in 100 mL distilled water and volume was made up to 1 L.

2.1.3 Standard EDTA solution (0.01 M):

0.01 M stock solution of the EDTA was prepared by dissolving 3.744 g disodium salt of EDTA in 1 L deionized water. The stock solution of EDTA was standardized against a standard lanthanum chloride in presence of 15 mL of 50% aqueous solution of sulphosalicylic acid and 30 ml of 30% hexamine solution at pH 5.6 using xylenol orange as indicator.

2.1.4 Thorium nitrate (0.01 N):

0.01 N stock solution of thorium nitrate was prepared by dissolving 1.3806 g of high purity thorium nitrate tetrahydrate salt in 1 litre deionized water.

2.1.5 Flux:

Flux was prepared by thoroughly mixing high purity 1 g reagent grade sodium carbonate and 0.5 gm zinc oxide.

2.1.6 Colour Reagent:

Color reagent was prepared freshly each time by mixing in the sequence, 10 mL of 0.2 N hydrochloric acid, 10 mL aqueous solution of 2% hydroxylamine hydrochloride, 10 mL Alizarine sodium monosulfonate, 40 mL of 0.1% aqueous solution and 40 mL of 0.05% aqueous solution of thorium nitrate tetrahydrate, [Th(NO₃)₄.4H₂O],.

2.1.7 Other reagents:

Sulphosalicylic acid 50% (v/v), Hexamine 30% (v/v), Xylenol Orange 0.1% (w/v) were freshly prepared as per requirements.

2.2. Sample dissolution

0.2 g of well ground 100-mesh glass sample dried at 105-110°C was mixed thoroughly with 1 g. of flux in a platinum crucible. The sample was heated for 30 minutes at 900°C in muffle

furnace. After cooling 30 mL deionized water was added to it and crucible along with fused mass was kept on hot plate at a controlled temperature for 1 h to dissolve the soluble materials. It was heated on hot plate at a controlled temperature for 1hr to dissolve the soluble materials. Then the whole material was transferred in cleaned glass beaker with a clean glass rod and it was heated for 10 minutes to dissolve the water-soluble contents. The suspension was transferred into 25 mL centrifuge tube fitted with stopper and the suspension was centrifuged for few minutes to separate solids from liquid. The supernatant liquor removed by mean of teat pipette. The process of heating and centrifuging repeated several times to leached out fluorine completely from the suspension. The precipitate was filter through Whatman filter paper No. 40 and washed several times with 0.1% sodium carbonate solution. The final solution was made 100 mL by deionized water. After filtration 1 ml of (1:3) hydrochloric acid was added to the solution and shaking vigorously to expel the carbon dioxide. The final volume was made 100 mL by deionized water.

2.3 Determination of fluorine

From the stock solution 10 mL aliquot was Pipette out and 15 mL of 50% aqueous sulphosalicylic acid add sufficient 30% hexamine solution was added to get pH 5-6, and to mask traces of aluminium left in the solution. Further 25 mL standard Lanthanum chloride solution was added and it was boiled for few minutes to react with fluorine present in the solution. The excess unconsumed lanthanum was than back titrated with EDTA using xylenol orange as indicator. The amount of fluorine content can be easily calculated from the amount of lanthanum consumed (1g lanthanum = 0.4118 g Fluoride). For comparison the acceptance of the described method, the amount of fluorine present in the sample was also determined by the slightly modified spectrophotometric method after extraction of fluorine by the distillation method [4]. This modified method is based on the principle of bleaching the thorium-alizarin lake by fluorine. In this method the aliquots containing known quantity of fluoride ion were taken into 50 mL volumetric flask. Standards containing 0, 10, 20, 30, 50 and 500 mgL⁻¹ of fluoride ion were prepared for each series of assays. 5 mL of colour reagent were added to each flask and volume was made up to the mark with distilled water, shaken and allowed to stand for 2 hours. The absorbance was measured at 520 m μ , from the calibration graph the amount of fluorine present in the samples were calculated. It is observed that the results obtained by both methods were comparable.

3. Results and discussion

3.1. Reproducibility

The method proposed based on titrimetry is a rapid and easy method in comparison to the existing reported methods. The mixture of zinc oxide and sodium carbonate forms water-soluble salts of fluorine. While at high temperature, the other constituents like alumina, calcium oxide and magnesium oxide do not form water-soluble salts. The chemical analysis of the glass samples at various pH and fusion temperature are shown in Table 1. It has been found that on fusion the samples even at 950 °C for 30 minutes, there is no loss of fluoride ion. In the proposed method, pH has a crucial role because; at pH ≤5 hydrogen ions form fluoride species like HF_2^- and undissociated HF. Therefore the pH of the solution is adjusted to 5.5 to 6.5 by using sulphosalicylic acid and hexamine. The analytical data shows that the results are more reproducible when samples are fused at temperature 950 °C and measurement are carried out at pH 5.5.

Table 1. Effect of fusion temperature and pH on the determination of fluorine contents for sample no. 1

Variation of pH (Sample fused at 900 °C)	% F	Variation of fusion temperature (at fixed pH 5.5)	% F
7	0.95	1050 °C	1.12
6.5	1.27	1000 °C	1.20
6	1.29	950 °C / 900 °C	1.35
5.5	1.35	800 °C	1.25
4	1.02	700 °C	1.08

3.2. Interferences

Al, Fe and Si form complexes with fluorine, the use of sodium carbonate and zinc oxide flux allows their ions to be retained as an insoluble residue in the filtrate. Any aluminum, titanium left in the filtrate is complexed by sulphosalicylic acid and hexamine. Since the distillation method is lengthy and involves the use of elaborate apparatus, whereas the proposed method requires no special apparatus and the proposed method also removes all the interfering elements likely to be present in glass sample like the distillation method. Moreover the selection of lanthanum as complexing agent for fluoride ion has great advantage because

normally glass sample does not contains lanthanum so there is no risk of interference or error from the sample itself in the result.

Several synthetic solutions are prepared containing varying amount of fluoride, Al and Ti and they are analyzed by following the method proposed. The analytical results (Table 2) shows that the sample contains up to 15% Al_2O_3 , than ≥ 0.04 % of fluoride can be measured without aluminum interference and if sample contains more than 0.1% fluoride ion up to 30% Al_2O_3 can be present without interference.

Table 2. Effect of foreign ions in the determination of fluorine

Synthetic solution no	Amount taken (%)			Found (%F)
	Al	Ti	F	
1.	15	0.40	0.05	0.048
2.	12	0.30	0.1	0.102
3.	25	0.90	0.15	0.17
4.	25	0.95	3	2.98
5.	30	1.0	5	5.02

3.3. Validation

The analytical results (% F based on sample weight of 200 mg) of few glass samples are given in Table 3. The result found by the method proposed is comparable with the results found by existing method. The proposed method was also applied to Standard Reference Materials NBS 91 in order to estimate the accuracy and precision of the method. The certified percentage of fluoride is 5.72, the analysis report in Table 4 showing a good agreement with the certified value.

Table 3. Comparison of the fluorine contents by the method proposed and existing methods

Glass Sample No.	Al found (%)		Result found (% F)	
	standard method	method proposed	modified spectrophotometry	existing method
1	12.15	1.35±0.09	1.33±0.12	1.39
2	18.23	1.19±0.08	1.17±0.10	1.15
3	15.79	1.14±0.08	1.12±0.10	1.15
4	20.88	2.05±0.10	2.08±0.12	2.04

Table 4. Analytical results of Standard Reference Material NBS 91

Certified value	Result found (% F)		
	method proposed	modified spectrophotometry	existing method
5.72	5.73±0.11	5.76±0.16	5.65±0.16

4. Conclusions

The proposed method is very simple and fast, as it does not require any separation or distillation. A wide range of fluoride ion from 0.4 to 6% can be measured successfully by this method in presence of up to 30% of Al₂O₃ without any interference.

Acknowledgements

The author wishes to thank NPL and CGCRI to carry out the work.

References

1. Willard H H and Winter O B (1933) Volumetric method for determination of fluorine. *Ind Eng Chem* 5:7.
2. Shell H R and Craig R L (1954) Determination of silica and fluoride in fluorosilicates. *Anal Chem* 26: 996.
3. Cumming A C and Kay S A, *Quantitative chemical analysis*, 8th Edn, London, Gurney and Jackson, P 186.

4. Dasgupta S and Roy S K (1985) Chemical analysis of ceramics and allied materials, 1st Edn, Indian Institute of Ceramics, Kolkata, Ganguli and Kumar, P 116.
5. Newman A C D (1968) A simple apparatus for separating fluorine from aluminosilicates by pyrohydrolysis. *Analyst* 93: 827.
6. Berns E G and Vander Zwaan P W (1972) The pyrohydrolytic determination of fluoride, *Anal Chim Acta* 59: 293.
7. Madden J E and Haddad P R (1999) Critical comparison of retention models for the optimisation of the separation of anions in ion chromatographyII. Suppressed anion chromatography using carbonate eluents. *J Chromatogr A* 850: 29.
8. Peters M A, Ladd D M (1971) Determination of fluoride in oxides with the fluoride-ion activityelectrode. *Talanta* 18: 655.
9. Oliver R T and Clayton A G (1970) Direct determination of fluoride in miscellaneous fluoride materials with the orion fluoride electrode. *Anal Chim Acta* 51: 409.
10. De Mayer E A P and Verbeeck R M H (1998) Analysis of bioactive fluoride-containing calcium aluminosilicate glasses. *Anal Chim Acta* 358: 79.
11. Hall A and Walsh J N (1969) A rapid method for the determination of fluorine in silicate rocks and minerals. *Anal Chim Acta* 45: 341.
12. Huang, W H and Johns W D (1967) Simultaneous determination of fluorine and chlorine in silicate rocks by a rapid spectrophotometric method. *Anal Chim Acta* 37: 508.
13. Pablos A de, Fernández Navarro J M and Valle F J (1998) Contribution to the chemical analysis of fluorophosphate glasses. *Glass Technol* 39: 100.
14. Simmingskold B (1997) Raw materials for Glass Melting. Eds Teison K H and Wright R D, Society of Glass Technology, Sheffield, UK.
15. Allison R S (1953) Determination of small amounts of fluorine in glass. *J Soc Glass Tech* XXXVII P 213.
16. Yamamura S S, Wade M A and Sikes J H (1962) Direct spectrophotometric fluoride determination. *Anal Chem* 34: 1308.
17. Vogel I A (1982) A textbook of quantitative inorganic analysis 4th edn (Longmann, London).

Received: November 23, 2007; Accepted: December 28, 2007

Corresponding author: Nahar Singh

Address: Analytical Chemistry section, National Physical laboratory, Dr K.S. Krishnan Marg,
New Delhi-12

Phone: +91-11-25742609 to 613 Extn. 2397

Fax: +91-11-25726938, 25726952

Email: naharsingh@mail.nplindia.ernet.in