

HIGH-FREQUENCY TITRATION

COMMUNICATION 6. DETERMINATION OF FLUORINE IN FLUOROPOLYMERS CONTAINING AND FREE FROM CHLORINE*

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Titrimetric methods are known for the determination of fluorine [1-8] in fluoroorganic compounds, in particular in fluoropolymers containing chlorine and free from the latter, after the samples have been mineralized. Titration is carried out with a solution of thorium nitrate using sodium alizarin sulfonate as the indicator. The drawback of these methods is the necessity of keeping the pH of the solution within narrow limits (2.9-3.0), and also the difficulty of establishing the color change at the equivalence point.

The most interesting method for the microdetermination of fluorine in fluoropolymers is a high-frequency titration method suggested by Monand [9] for the determination of fluorine in fluoroorganic materials after mineralization of the latter. According to this method, an aliquot of the fluoroorganic compound is rapidly burned (at 1150°) in a platinum boat in a stream of oxygen. The gaseous combustion products are passed through a quartz tube containing platinum, in the form of two spirals, as a catalyst. The fluorine thereby reacts with the quartz of the tube: $4F + SiO_2 \rightarrow SiF_4 + O_2$. In the presence of organic compounds containing hydrogen the following reaction occurs: $RF_4 + SiO_2 + nO_2 = nCO_2 + nH_2O + SiF_4$. The silicon fluoride is hydrolyzed in aqueous solution according to the equation: $SiF_4 + 2H_2O \rightarrow 4HF + SiO_2$.

TABLE 1. Titration of Fluorine in Sodium Fluoride (45.25% F)

Aliquot, mg	Fluorine found, %	Error, %	Aliquot, mg	Fluorine found, %	Error, %
10,02	45,65	+0,40	11,45	45,27	+0,02
20,25	45,20	-0,05	11,02	45,25	+0,02
10,50	45,22	-0,03	10,90	45,72	+0,47
10,75	44,83	-0,32	10,30	44,80	-0,45
11,00	45,27	+0,02	10,40	44,93	-0,22

The fluoride ions formed (for fluoride concentrations not less than 1 mg in 10 ml of solution) are determined by high-frequency titration using 0.02 N strontium acetate as titrant.

On checking this method we found that at the strontium acetate concentration indicated, and also at higher concentrations, a precipitate of strontium fluoride is not formed. Because of this we therefore chose 0.05 N calcium acetate as titrant, since calcium fluoride is less soluble than strontium fluoride, and this enables the equivalence point to be determined more accurately.

We first of all established the optimum conditions for carrying out high-frequency titration with an accuracy of $\pm 0.5\%$, on synthetically prepared solutions of NaF and NaCl, containing 0.90-1.3 mg F in 10 ml of solution, and for chloride contents not greater than 2.5 mg in the same volume (Table 1). The method was then applied to the analysis of fluoropolymers containing chlorine, and also free from the latter.

Combustion of the fluoropolymers was carried out by the Schoniger method in a sealed flask filled with oxygen [6-8, 10-11], the gaseous products being absorbed with 0.5% sodium acetate solution. The normality of the $Ca(CH_3COO)_2 \cdot H_2O$ was established against pure Na_2CO_3 or pure sodium fluoride, high-frequency titration being used again. Table 2 shows that the experimental error for fluorine in fluoropolymers is not greater than 1%. We determined

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TABLE 2. Determination of Fluorine in Fluoropolymers

Test material	Fluorine found, %	
	titration with $\text{Th}(\text{NO}_3)_4$ using alizarin red S	high-frequency titration with $\text{Ca}(\text{CH}_3\text{COO})_2$
Polymer 1	63.49	63.60
	63.74	63.92
Polymer 2	53.85	53.70
	54.06	54.17
Polymer 3	54.88	54.05
	54.50	54.52
Polymer 4	65.45	66.18
	64.89	65.30
Polymer 5	64.50	64.35
	64.03	64.17
Polymer 6	53.86	53.08
	53.17	54.00

TABLE 3. Titration of 65 ml of 0.0048 N Sodium Fluoride Solution (After Mineralization of 9 mg of Fluoropolymer) with 0.05 N Calcium Acetate Solution

0.05 N $\text{Ca}(\text{CH}_3\text{COO})_2$ added, ml	Microammeter reading, μA	Time between successive additions of titrant, min
0	50	—
3.0	53	1
4.5	50	1
5.0	48	1
5.5	48	3
6.0	47	3
6.5	47	1
7.0	48	15
7.5	49	15
8.0	50	15
8.5	52	15

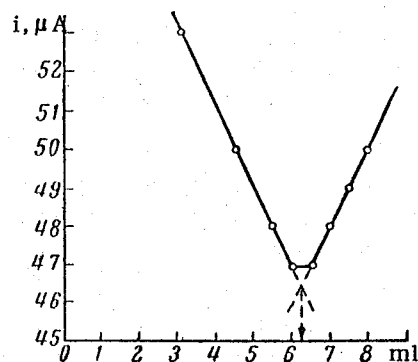
The temperature of the solution is adjusted to 65-67° by pouring heated distilled water into the cell until the level of the solution is not higher than 2-3 mm above the edge of the upper screened cover of the cell. Titration is carried out at a sensitivity of "5" on the apparatus.

The titrant is added in an amount equivalent to half the fluoride ion content at the beginning of a titration; it is subsequently added in 0.5 ml portions, and the titration suspended for the time intervals indicated in Table 3 between addition of each portion of titrant.

The values given in Table 3 are plotted on a curve. The fluorine content is calculated by means of the formula:

$$\% F = \frac{(V - V_0) 0.00095 \cdot 100}{g},$$

where V is the volume in ml of calcium acetate solution used for titrating an aliquot of fluoropolymer; V_0 is a correction to be applied to the titration results and which depends on the sensitivity of the apparatus under the given conditions; it is equal to 0.25 ml of 0.05 N calcium acetate; 0.00095 g is the amount of fluorine corresponding to 1 ml of 0.05 N calcium acetate solution; g is the weight of fluoropolymer taken.



High-frequency titration curve of 65 ml of 0.0048 N sodium fluoride (after mineralization of 9 mg of a fluoropolymer) with 0.05 N calcium acetate.

the fluorine content of fluoropolymers, after their combustion, by two methods: a) by a method developed by Lebedeva et al [6]; and, b) by our high-frequency method in which a correction is introduced for the sensitivity of the apparatus (Table 2).

It was found that readily reproducible results are also obtained with production samples of fluoropolymers containing up to 17% of chlorine.

Determination of Fluorine

An aliquot of fluoropolymer is wrapped up in filter paper and ignited in a platinum mesh basket in a 500-ml flat-bottomed quartz flask. Ten ml of 0.5% sodium acetate to which 15-20 ml of water has been added is used as the absorbent liquid. The contents of the flask are shaken until the mist has disappeared. The solution in the flask is boiled for 3-5 min. The hot solution is neutralized with 0.05 N sodium hydroxide using phenol red (0.04% solution) as indicator, and a small excess of sodium hydroxide added (a few drops) until the color of the solution changes to raspberry. The hot solution is quantitatively transferred to the cell of a high-frequency apparatus of the VU-IA type from GEOKhI AN SSSR [12].

The amount of sample taken should be varied between 9-12 mg, depending on the percentage content of the test polymer. Thus, for polymers not containing chlorine, an aliquot of 9-10.5 mg is recommended, while for polymers containing chlorine, 10.5-12 mg should be taken.

SUMMARY

A method has been developed for the determination of fluorine in fluoropolymers containing chlorine. It is based on high-frequency titration of fluoride with calcium acetate after mineralization of the samples. The experimental error is $\pm 1\%$, while one determination takes about 1 h.

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