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Abstract

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ON THE DETERMINATION OF FLUORINE AND CHLORINE IN POLYMERS BY THE GAMMA-ACTIVATION METHOD

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A large number of works have been devoted to the determination of fluorine and chlorine in organic compounds. In a number of them, rapid methods for determining halogens directly in polymers have been described [1,2]. Most of the indicated methods are based on decomposition of a sample of the substance being analyzed. The universality of the methods is often determined by the type of chemical bond of the halogen in the compound. Thus, for a number of fluorine-containing polymers such methods are very difficult to use because of their high stability [3].

From this point of view, the radioactivation method of analysis is promising. In work [4], a method of activation analysis of fluorine in organic compounds by the reaction $F^{19}(n,\gamma)F^{20}$ is described. Identification of fluorine was carried out by its radioisotope F^{20}, emitting gamma quanta with an energy of 1.63 MeV. Irradiation of the analyzed samples was carried out in the central zone of a reactor at a thermal-neutron flux of $\sim 10^{12}$ neutrons/(cm$^2 \cdot$ s). Because of the short half-life of the isotope F^{20}, equal to 10.3 s, it was necessary to use pneumatic mail for rapid delivery of the irradiated samples to the counting setup, which considerably complicated the analytical procedure. The accuracy of the analysis was 1-2% relative.

For activation analysis of fluorine and chlorine in organic compounds, and above all in polymers, photonuclear reactions can be successfully used along with neutron reactions. The proposed method is based on the use of the reactions: $F^{19}(\gamma,n)F^{18}$ and $Cl^{35}(\gamma,n)Cl^{34}$. The F^{18} and Cl^{34} formed in these reactions are positron-active isotopes and have half-lives of 112 min and 33 min, respectively.

As the radiation source, the betatron of the Physicochemical Institute named after L. Ya. Karpov was used, with bremsstrahlung energy adjustable from 4 to 25 MeV and an intensity of 50 r/min at a distance of one meter from the target. The betatron is equipped with a special device—a "pocket" [5]—which permits samples to be irradiated inside the accelerating chamber of the betatron. The intensity of bremsstrahlung inside the "pocket" was $\sim$ 6000 r/min.

The measurement of the induced activity of the samples was carried out on a

setup registering gamma quanta arising during positron annihilation. The setup consisted of two scintillation counters (NaI(Tl) crystals and FEU-29 photomultipliers), registering two annihilation gamma quanta with an energy of 0.511 MeV flying apart in opposite directions, two preamplifiers, amplifiers and single-channel analyzers (two LAS units), a coincidence-circuit unit (“yoke” setup), making it possible to record both gamma quanta in the channels as one event, and a mechanical recorder.

Both irradiation and measurement of the activity of the samples were carried out in a strictly fixed geometry [6].

As standards, tablets 6 mm in diameter and 1.7 mm thick, prepared from LiF and NaCl, were used. The dimensions of the analyzed polymer samples were identical; the weight was ~ 100 mg. The correction for the dose received by the samples (standards) in parallel experiments was determined

by the magnitude of the induced activity of two thin silver plates (monitors) placed on both sides of the sample tablet and irradiated simultaneously with it.

Since the threshold of photonuclear reactions on fluorine and chlorine ($\sim$ 10 MeV) is appreciably lower than the threshold for carbon (18.6 MeV), in order to exclude activation of the latter, irradiation of the samples was carried out at a maximum bremsstrahlung energy of 18 MeV.

The irradiation time of the sample was 20 min. Measurement of the induced activity was carried out according to a definite time program: three measurements, each lasting 5 min, with an interval of one minute for the sample and the monitor, respectively.

The unknown concentration was determined from the formula:

$$C_x = C_{\text{st}} \frac{A_x}{A_{\text{st}}} \cdot \frac{D_{\text{st}}}{D_x} \cdot \frac{P_{\text{st}}}{P_x},$$

where C_x and C_{st} are the concentration of fluorine or chlorine in the analyzed sample and in the standard, respectively. A_x and A_{st} are the induced activities (F or Cl) in the sample and the standard. D_{st}/D_x is the ratio of the dose values received by the standard and the sample, determined from the activity of the monitor. P_{st}/P_x is the ratio of the weight of the standard to the weight of the sample.

For the simultaneous determination of fluorine and chlorine in one sample from the measurement of the total induced activity, a special analytical procedure was developed. Starting from the exponential form of the law of radioactive decay, one may write, for a system consisting of components A and B, two equations for the time instants t_1 and t_2.

$$-\left[\frac{d(A+B)}{dt}\right]_{t=t_1} = A_0\lambda_A \exp(-\lambda_A t_1) + B_0\lambda_B \exp(-\lambda_B t_1) = N$$

$$-\left[\frac{d(A+B)}{dt}\right]_{t=t_2} = A_0\lambda_A \exp(-\lambda_A t_2) + B_0\lambda_B \exp(-\lambda_B t_2) = M, \qquad (1)$$

where λ_A and λ_B are decay constants, and A_0 and B_0 are the activities of each of the components at the initial moment of time.

Table 1

Type of sample	Substance	Element determined	Percentage content of element, calculated	Percentage content of element, found	Number of determinations	Relative standard error of a single measurement (sample), δ, %	Total standard error $\delta(\%) = \sqrt{\delta^2_{\text{sample}} + \delta^2_{\text{st}}\%}$	Deviation from theoretical value (rel.
Standards	LiF	F	73.25	–	4	0.59	–	–
Standards	NaCl	Cl	60.66	–	4	1.41	–	–
Analyzed samples	$(-CF_2-CF_2-)_n$	F	75.98	75.09	5	0.35	0.69	1.17
Analyzed samples	$(-CH_2-CHCl-)_n$	Cl	56.75	57.45	5	0.38	1.46	1.23
Analyzed samples	$(-CF_2-CFCl-)_n$	Cl	30.44	30.52	4	2.14	2.56	0.26
Analyzed samples	$(-CF_2-CFCl-)_n$	F	48.94	48.21	4	1.34	1.46	1.49

From these equations one can obtain expressions for A_0 and B_0:

$$A_0 = \frac{N\exp(-\lambda_B t_2) - M\exp(-\lambda_B t_1)}{\lambda_A\left[\exp(-\lambda_A t_1) - \lambda_B t_2 - \exp(-\lambda_A t_2 - \lambda_B t_1)\right]},$$

$$B_0 = \frac{M\exp(-\lambda_A t_1) - N\exp(-\lambda_A t_2)}{\lambda_B\left[\exp(-\lambda_A t_1 - \lambda_B t_2) - \exp(-\lambda_A t_2 - \lambda_B t_1)\right]}. \qquad (2)$$

The quantities N and M are determined experimentally according to a preselected time program for measuring the induced activity of the sample. The optimum value of $\Delta t = t_2 - t_1$ can be obtained from the condition that the first derivative with respect to t_2 of the quantity in the numerator of the expression for A_0 and B_0, with the values of M and N substituted from equations (1), i.e., from the determinant of this system of equations, be equal to zero. After simple transformations one obtains:

$$\Delta t = t_2 - t_1 = \frac{1}{\lambda_B - \lambda_A} \ln \frac{\lambda_B}{\lambda_A}. \tag{3}$$

The method described above was tested on a number of known polymers of technical purity; the results of the analysis are summarized in Table 1.

As can be seen from the data in Table 1, the magnitude of the error in the determination of chlorine considerably exceeds that for fluorine. This is due to the relatively low cross section of the photoneutron reaction on Cl^{35} in comparison with F^{19} in the energy interval of bremsstrahlung used. The accuracy of chlorine determination can be improved by increasing the weight of the samples analyzed.

It should be noted that an analogous method can be used for the simultaneous determination of C and F, C and Cl, and a number of other elements.

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named after L. Ya. Karpov

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