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# Determination of Fluorine in Organic Functional Materials

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## Abstract

For the analysis of fluorine in difficult-to-burn and complex organofluorine compounds, special additives have been developed to ensure complete decomposition of the substances. Using a spectrophotometric technique based on the formation of a fluoride complex with lanthanum alizarin complexone various organofluorine compounds have been analyzed with fluorine content of 1.5 to 70 % containing heteroelements in their structures: sulphur, chlorine, bromine, phosphorus, boron, selenium, tellurium in various combinations, as well as metals. The error of determination was established to be not higher than 0.5 abs. %

**Keywords:** organofluorine compounds, lanthanum alizarin complexone, fluorine determination

## INTRODUCTION

The Novosibirsk Institute of Organic Chemistry is named after Academician N. N. Vorozhtsov, a founding figure in the chemistry of polyfluorinated compounds in the USSR, who was the first Director of this Institute. This is why attention to fluorine chemistry, synthesis and therefore analysis of organofluorine compounds was one of the key issues at the institute, even at the stage of establishment.

Primary interest in organofluorine compounds, having emerged early in the XX century, was exclusively the privilege of fundamental science. However, development of these studies has resulted in so rapid growth of the practical applications of organofluorine substances that it is now difficult to imagine doing without them in the past. These substances include fluorinated rubber and teflon, surfactants and chladones, artificial blood and anaesthetics, surpassing lubricants, new medicines, pesticides and many others. In addition, organofluorine compounds still serve as the objects to study the fundamental theoretic problems of chemistry: the nature of saturated and hydrogen bonds, reaction mechanisms, the nature of intermolecular forces, *etc*.

The methods of detection and quantitative analysis of these compounds, in particular determination of fluorine content in them, were also developing with high intensity. The reactivity of organofluorine compounds is often substantially different from that of their non-fluorinated analogues, which brings complications into a priori predictions of their chemical behaviour. To analyze an organofluorine compound, most typically it is necessary to break a C–F bond and to obtain fluorine in the form of the anion. The high energy of C–F bond, as well as the dense and voluminous shell of F atoms isolating the carbon chain from external chemical actions, promote high thermal and chemical stability of organofluorine compounds. For this reason, their mineralization requires special severe conditions.

Depending on the nature of organic compound, various sample preparation methods have been

described: alkali fusion in a crucible or microbomb [1], combustion in a flask filled with oxygen (Shöniger method) [2], microwave decomposition [3], pyrolytic combustion in a tube with oxygen flow [4], reductive decomposition in low-temperature plasma [5]. A simple automated system based on combustion followed by pyrohydrolysis was proposed in [6].

There are many methods for the quantitative determination of fluorine in the form of fluoride ion, and a review of these methods is presented in [7]. The most widespread methods among them are spectrophotometry and the use of ion-selective electrodes, firstly due to economic reasonableness and simplicity, broad introduction into laboratory practice, secondly, because of the sufficient (in the majority of cases) selectivity and sensitivity. However, as demonstrated in the review, other (almost all known) analysis methods were also used. For example, during the recent years, along with the classical methods involving preliminary decomposition of the substance, methods have been developed in which the decomposition stage is directly combined with the measurement of the analytical signal. In addition, non-destructive physical methods of elemental analysis are under development and broad application: X-ray phase analysis, nuclear magnetic resonance (NMR), neutron activation analysis, *etc*., but these methods do not always meet the requirements of researchers in organic chemistry [8–14]. The choice of a method depends on the requirements imposed on the analysis. In some cases, the low detection limit is essential, while in other cases rapid and economic procedures are needed, or the absence of matrix effects, *etc*.

The goal to develop the methods for the analysis of organofluorine compounds meeting all the requirements of researchers in organic chemistry had been put forward for the analytical laboratory of the NIOCh, headed at that time by L. N. Diakur. In the 1960s, methods of classical gravimetric analysis of carbon and hydrogen modified for use with thermally stable fluorinated compounds had been successfully introduced [15]. A complicated and labour-intensive method of nitrogen determination according to Dumas was replaced by the analysis with the help of an automatic CHN analyzer Hewlett-Packard, model 185 [16]. However, indirect method of fluorine determination in organic compounds, which was in use during those years in the laboratory, based on attenuation of colouring of the thorium-arsenazo complex during the interaction with fluoride ion [17], did not always meet the requirements in accuracy and sensitivity. It was necessary to develop a direct, accurate and universal analysis method, and this task was successfully fulfilled, supervised by V. P. Fadeeva [18].

This article presents the experience accumulated over many years in the application of the method of fluorine determination in organofluorine compounds of different classes, including functional materials and their precursors, developed at the Laboratory of Microanalysis in the NIOCh SB RAS. This method is based on the spectrophotometric determination of fluorine in the form of a complex with lanthanum-alizarin complexone after combustion of the substance in a flask filled with oxygen (according to Shöniger).

## EXPERIMENTAL

### *Reagents and solutions*

The reagents used in the measurements of the mass fraction of fluorine were: lanthanum (III) nitrate hexahydrate ($7 \cdot 10^{-4}$ M), alizarin complexone (AC, *initial and working solutions*), sodium carbonate trihydrate and glacial acetic acid (to prepare a buffer solution with pH 4.5), ammonia, ethanol, phenolphthalein, sodium hydroxide (10 %), potassium nitrate (saturated solution). All reagents were of analytical-grade purity.

Preparation of the *initial solution* of AC. Distilled water in the amount of 150 $cm^3$ and 0.25 $cm^3$ ammonium were added to the weighted portion 0.308±0.001 g of AC in a conical flask with the volume of 500 $cm^3$, the flask was placed in a water bath at a temperature of 50±2 °C for 30 min under permanent mixing. Glacial acetic acid 0.25 $cm^3$ was poured into the hot solution. After cooling to room temperature, the mixture was filtered into a volumetric flask of 200 $cm^3$, and distilled water was added to the mark.

Preparation of the *working* $8 \cdot 10^{-4}$ *M solution* of AC. Acetate buffer solution with pH 4.5, 200 $cm^3$, and 150 $cm^3$ of ethanol were added to 200 $cm^3$ of the initial AC solution in the volumetric flask 1 $dm^3$ in volume. Distilled water was added to the mark, and thorough mixing was performed. The resulting solution is stable and ready to use for not less than 1 year.

### *Sample preparation*

The method of decomposition in a flask filled with oxygen (according to Shöniger) [2] is pre-

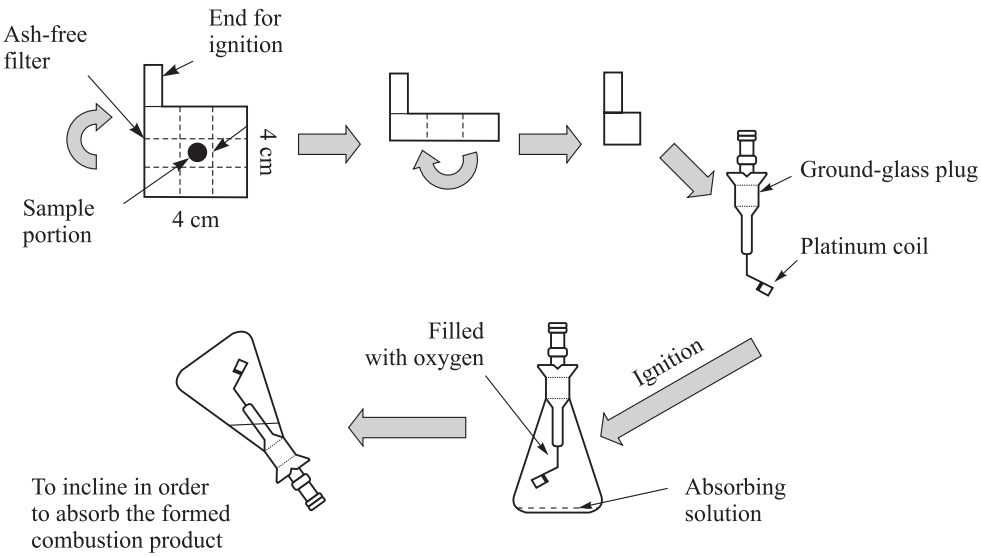



Fig. 1. Schematic of the method involving combustion in a flask filled with oxygen (according to Shöniger).

sented in Fig. 1. A weighted portion of the sample for investigation was 1–3 mg. Combustion was carried out in gaseous oxygen with the purity of 99.7 %. Sample holder was made of a platinum wire (∅ = 0.6–1.0 mm) with 99.99 % purity. Heat-resistant Erlenmeyer flasks 500 mL in volume, glass plugs with a glass bar and a platinum wire 15 cm long sealed into the bar were employed; the end of the wire was coiled by 5 cm. The absorbing solution was distilled water without any additives. Fluorine is completely absorbed in the form of fluoride ion within 30 min after combustion, in a refrigerator at a temperature of 8–10 °C.

### *Plotting the calibration graph*

After complete absorption of the gases formed during combustion, the absorbing solutions are neutralized with 10 % NaOH solution with respect to phenolphthalein, transferred quantitatively into the flasks 250 $cm^3$ in volume, and distilled water is added to the mark. Then 5, 10 and 15 $cm^3$ of each initial solution are introduced into a volumetric flask 100 $cm^3$ in volume, 25 $cm^3$ of AC solution and 25 $cm^3$ of $La(NO_3)_3$ solution are added, distilled water is added to the mark, and the corresponding content of fluoride in 1 $cm^3$ of the working solutions is calculated.

The solutions were thermostated for 30 min, and the dependence of their optical density on fluorine concentration is measured at the wavelength of 618 nm in 1 cm cell (calibration graph), which is then used to determine fluorine in the compounds under investigation.

To plot the calibration graphs, standard substances with the known fluorine content were used: pentafluorobenzoic acid ($C_7HF_5O_2$, CAS 602-94-8) with 99.9 % purity (% F = 44.8±0.5) and 4-fluorobenzoic acid ($C_7H_5FO_2$, CAS 456-22-4) with 99.9 % purity (% F = 13.56±0.5).

### *Equipment*

Measurements were carried out using a Cary-60 spectrophotometer (Australia). The samples were weighed using Mettler Toledo AT20 microanalytical balance (Switzerland). Analytical solutions were prepared using Sartorius CP224S analytical balance (Germany).

## RESULTS AND DISCUSSION

The unique reaction of fluoride anion with the lanthanoid AC complex is known as one of the most reliable methods of fluoride determination in aqueous solutions. It was proposed in the early 1960s [19].

In addition to practical significance, this reaction is of interest as a rare example of strong and highly selective spectral changes caused by the anion binding with the metal complex, which has not got a clear explanation yet. Colour change from red to blue resulting from the addition of fluoride ion to the equimolar mixture of lanthanide cation and AC is observed in weakly acidic acid (pH 3–5) and is significant only for La(III) and Ce(III). Significantly weaker spectral changes were revealed for heavier lanthanides, and start-

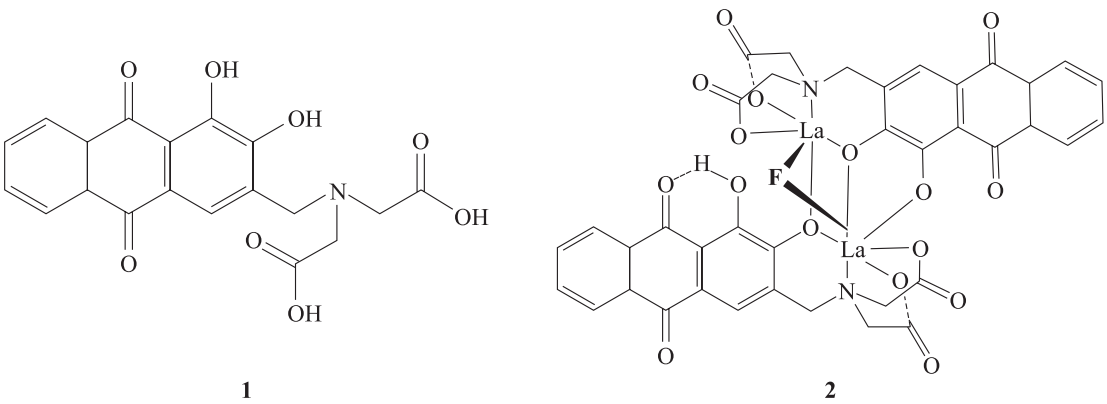



Fig. 2. Structure of alizarin complexone **1** and the complex of fluoride ion with lanthanum alizarin complexone **2**.

ing from Sm(III) no changes are observed. In view of the well-known close similarity of lanthanide cations, so strong selectivity to metal ion appears to be rather surprising, and its origin remains unclear. Rather inexplicit results were obtained in the earlier attempts to establish the composition of lanthanides – AC **1** and the complex of fluoride ion with lanthanum alizarin complexone **2**. Confirmation of the binary structure of this complex as shown in Fig. 2 was presented in [20].

Later on, photometric procedures for fluorine determination in various objects were developed on this basis [21–23]. It turned out that the procedures had some disadvantages, which brought complications into their application in routine analyses. Thus, in the majority of these procedures, it is proposed to use up to 70 % of organic solvents (isopropanol, acetone, dimethylsulphoxide or glycerol) in order to enhance the sensitivity of determination and to prevent hydrolysis of the fluoride complex. However, the use of large amounts of solvents is undesirable for serial analyses. For example, mixed working solutions of lanthanum alizarin complexone prepared using glycerol are stable only for 2 days. In addition, water-glycerol solution renders colour to spectrophotometric cells, which has a negative effect on the reproducibility of the results. Another disadvantage is the narrow range of fluorine concentrations from 0 to 40 μg within which Lambert–Beer's law is fulfilled.

With a four-fold increase in the amount of AC and lanthanum (III) nitrate taken for the formation of complex [18], a linear dependence of the optical density on concentration was obtained within the fluorine concentration range 0–100 μg/mL. The colour develops within 30 min, and colouring is stable for 48 h. In this situation, the use of organic solvents and glycerol is excluded, while the optimal reagent concentrations and analysis conditions are determined.

It should be stressed that AC purity is essential for the analysis [24]. Due to insufficient AC purity, lanthanum turns out to be in excess after mixing AC with lanthanum (III) nitrate hexahydrate at a ratio of 1 : 1, which leads to the formation of a double complex salt $AC \cdot La_2 \cdot H_2O$ and its precipitation. The purity of AC was controlled relying on data from elemental analysis.

To achieve complete decomposition of organofluorine compounds, the filter used to seal the weighted portion of the substance was impregnated by the saturated potassium nitrate solution, which allowed an increase in combustion temperature. In addition, for longer and more uniform combustion, polyethylene or glycerol was added to some samples. To take a portion of volatile or simply liquid substances, polyethylene capillaries were used; they were sealed with hot tweezers before packing in filter paper. The sensitivity of this method allows working with weighted portions of 1–3 mg, which is another factor promising the achievement of complete decomposition.

It is important that the calibration graph (Fig. 3) is to be plotted using the solutions obtained after combustion of a standard organofluorine compound, rather than standard solutions, for example sodium fluoride. This allows us to take into account the effect of all sample preparation factors on fluorine measurements, to minimize the matrix effect and to obtain better reproducible and accurate results. The mass fraction of fluorine (X, %) was calculated using equation

$$X = \frac{(C + \Delta C)V}{A} \cdot 100 \qquad (1)$$

where $C$ is the fluorine concentration determined from the calibration plot, mg/mL; $V$ is flask vol-

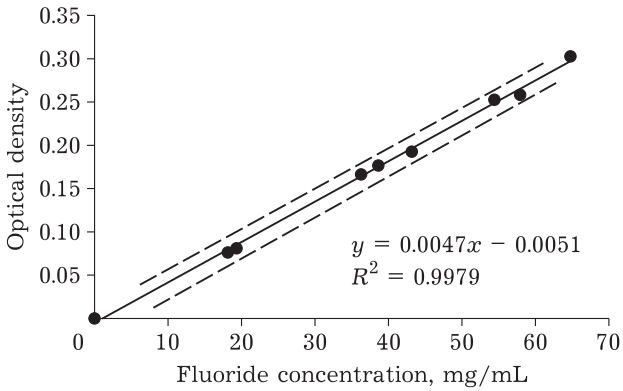



Fig. 3. Calibration graph to determine fluorine by means of spectrophotometry.

ume, mL; $A$ is the weighted portion of the sample, mg; $\Delta C$ is the error of the reference solution (correction), mg/mL.

$$\Delta C = C_1 - C_2 \quad (2)$$

where $C_1$ and $C_2$ are fluorine concentration in the reference solution, calculated from the weighted portion, and the same concentration determined from the calibration plot, respectively, mg/mL.

It should be stressed that this method requires everyday tests of the calibration characteristics over the standard substance to determine the correction (2), included in equation (1), because the actual calibration line (see Fig. 3) may shift from one day to another by approximately up to

TABLE 1

Results of fluorine determination in polyfluorinated arenes

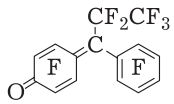
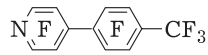
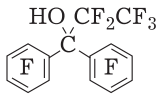
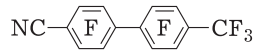
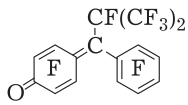
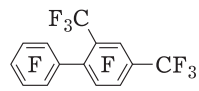
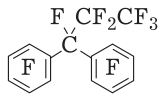
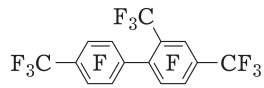
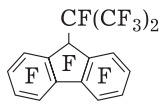
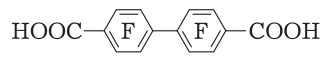
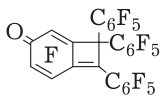
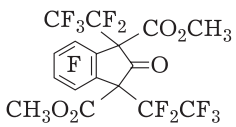
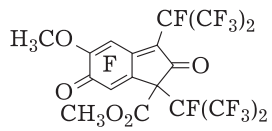
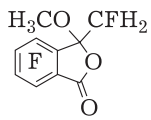
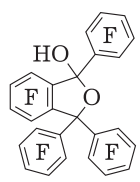
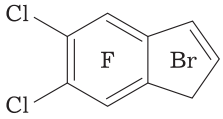
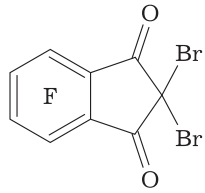
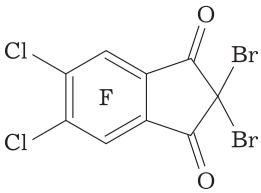
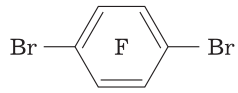
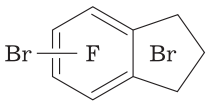
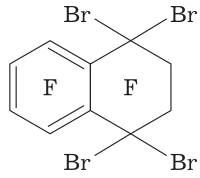
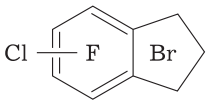
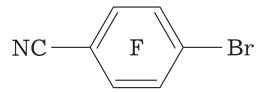
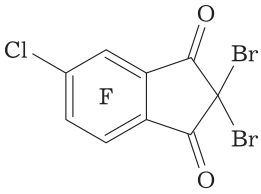
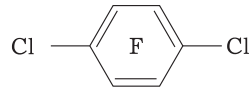
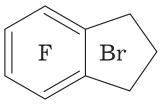
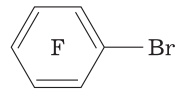
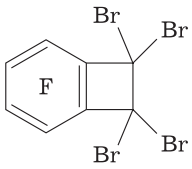
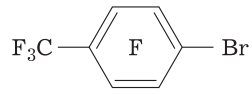
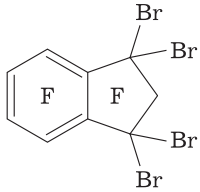
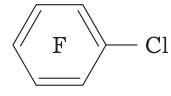
| Compound | Calculated according to the formula | Found | Compound | Calculated according to the formula | Found |
|---|---|---|---|---|---|
|  | 57.55 | 57.89 |  | 56.93 | 56.95 |
|  | 59.11 | 58.76 |  | 53.43 | 53.34 |
|  | 59.35 | 59.48 |  | 61.27 | 61.35 |
|  | 62.79 | 63.12 |  | 62.79 | 62.60 |
|  | 61.27 | 61.39 |  | 39.36 | 39.26 |
|  | 51.02 | 50.88 |  | 60.11 | 59.60 |
|  | 47.82 | 47.50 |  | 50.14 | 50.00 |
|  | 35.43 | 35.00 |  | 51.11 | 51. 11 |
|  | 52.97 | 52.60 | | | |

TABLE 2

Results of fluorine determination in chlorine- and bromine-containing polyfluoroarenes

| Compound | Calculated according to the formula | Found | Compound | Calculated according to the formula | Found |
|---|---|---|---|---|---|
|  | 7.08 | 7.06 |  | 21.03 | 21.04 |
|  | 9.29 | 9.20 |  | 24.18 | 24.26 |
|  | 10.09 | 10.16 |  | 25.67 | 25.59 |
|  | 10.95 | 10.84 |  | 29.32 | 29.17 |
|  | 14.25 | 14.35 |  | 34.01 | 34.19 |
|  | 15.08 | 15.16 |  | 38.70 | 38.93 |
|  | 15.45 | 15.23 |  | 44.33 | 44.48 |
|  | 20.21 | 20.09 |  | 46.91 | 46.29 |

±5 mg/mL, usually by ±(0.5–1) mg/mL (dash lines in the plot). We are unable yet to provide an explanation of this effect; however, it is impossible to obtain accurate results without taking into account this everyday correction.

The described analytical procedure has been in use at the Laboratory of Microanalysis of the NIOCh for a rather long time. Here we present some results obtained during the recent fives years.

TABLE 3

Results of fluorine determination in sulphur-containing polyfluoroarenes

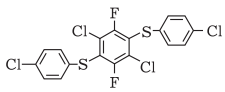
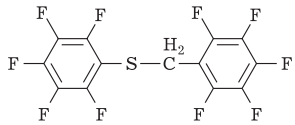
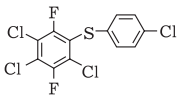
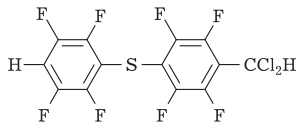
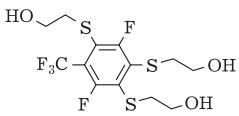
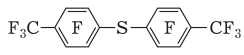
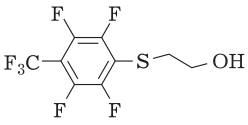
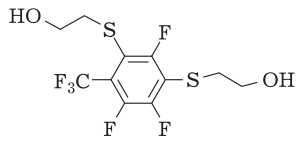
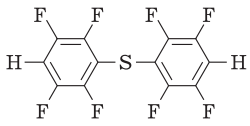
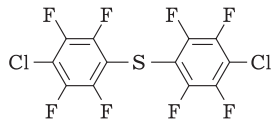
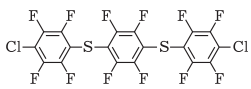
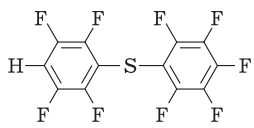
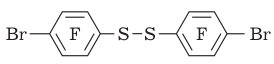
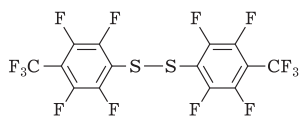
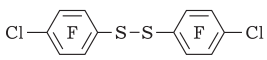
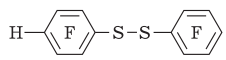
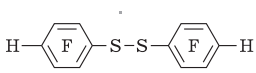
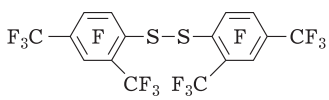
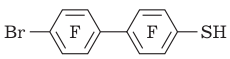
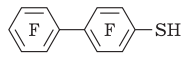
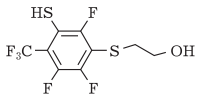
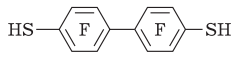
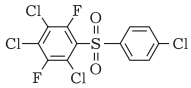
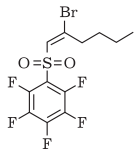
| Compound | Calculated according to the formula | Found | Compound | Calculated according to the formula | Found |
|---|---|---|---|---|---|
| | | | **Sulphanes** | | |
|  | 8.12 | 7.99 |  | 49.97 | 49.91 |
|  | 10.55 | 10.36 |  | 36.79 | 37.08 |
|  | 23.14 | 23.11 |  | 57.05 | 57.07 |
|  | 45.21 | 45.24 |  | 32.36 | 32.31 |
|  | 46.03 | 45.99 |  | 38.08 | 37.90 |
|  | 39.36 | 38.88 |  | 49.11 | 48.61 |
| | | | **Disulphanes** | | |
|  | 29.23 | 29.04 |  | 53.38 | 53.34 |
|  | 35.25 | 34.76 |  | 44.97 | 45.02 |
|  | 41.96 | 42.03 |  | 57.16 | 56.80 |
| | | | **Thiols** | | |
|  | 37.15 | 37.02 |  | 49.11 | 49.17 |
|  | 36.98 | 37.01 |  | 41.96 | 41.96 |
| | | | **Sulphones** | | |
|  | 9.69 | 10.00 |  | 24.16 | 23.80 |

TABLE 3 (Ending)

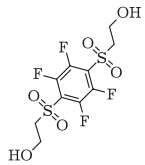
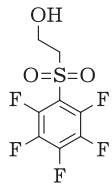
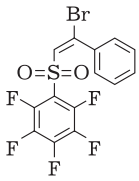
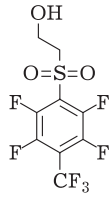
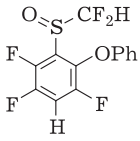
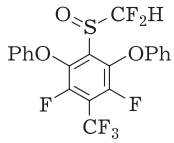
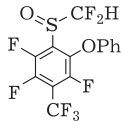
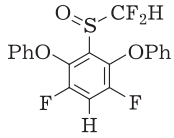
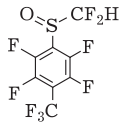
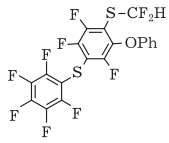
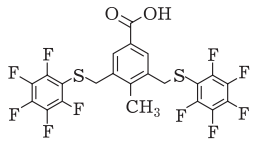
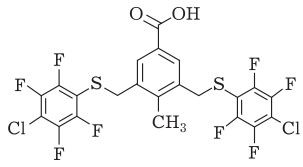
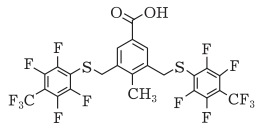
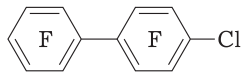
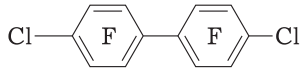
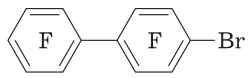
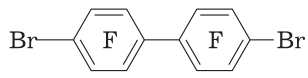
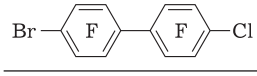
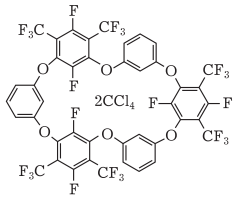
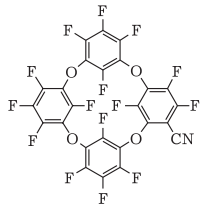
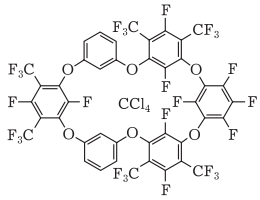
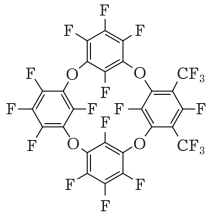
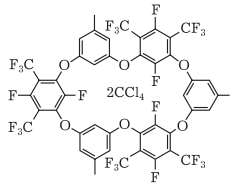
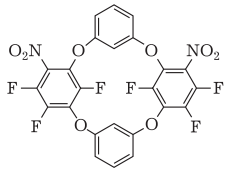
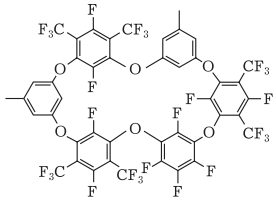
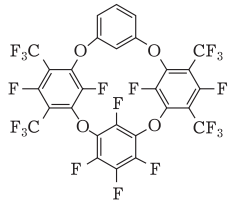
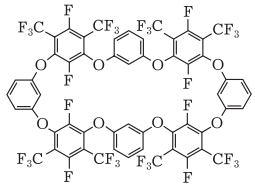
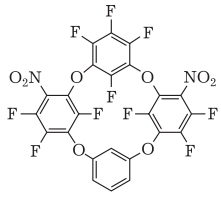
| Compound | Calculated according to the formula | Found | Compound | Calculated according to the formula | Found |
|---|---|---|---|---|---|
|  | 20.75 | 20.55 |  | 33.60 | 33.90 |
|  | 22.99 | 23.20 |  | 40.77 | 40.55 |
| **Sulphoxides** | | | | | |
|  | 29.48 | 29.30 |  | 28.61 | 28.65 |
|  | 38.95 | 39.04 |  | 19.17 | 19.14 |
|  | 54.09 | 54.39 |  | 37.67 | 37.88 |
| **Acids** | | | | | |
|  | 33.90 | 34.03 |  | 25.62 | 25.69 |
|  | 40.27 | 39.99 | | | |
| **Diphenyls** | | | | | |
|  | 48.77 | 48.79 |  | 41.41 | 41.50 |
|  | 43.29 | 43.07 |  | 33.34 | 33.08 |
|  | 36.94 | 37.05 | | | |

TABLE 4

Results of fluorine determination in calixarenes

| Compound | Calculated according to the formula | Found | Compound | Calculated according to the formula | Found |
|---|---|---|---|---|---|
|  | 33.13 | 33.19 |  | 42.97 | 42.85 |
|  | 41.11 | 41.12 |  | 20.24 | 50.17 |
|  | 32.16 | 31.96 |  | 20.13 | 20.09 |
|  | 45.52 | 45.26 |  | 42.67 | 42.52 |
|  | 42.67 | 42.65 |  | 29.76 | 30.10 |

Perfluorinated compounds are among the most difficult objects for analysis: the series of perfluorinated diphenyl alkanes, perfluorinated bi-, tri- and tetraphenyls, indanes with various substituents with fluorine content up to 63 wt. % (Table 1) [25–30], chlorine- and bromine-containing perfluoroarenes (Table 2) [31], sulphur-containing polyfluorinated arenes – sulphanes, disulphanes, thiols, compounds with sulphonyl and sulphinyl groups (Table 3) [32–38].

The practical significance of so interesting compounds as calixarenes (Table 4) is due to their unusual structure and involves their ability to undergo selective complexation [39–41].

The structure of 1,4-naphthoquinone often occurs in many synthesized and natural compounds exhibiting antibacterial, antifungal, antiviral, antitumour and antimalarial action. Polyfluorinated functionalized 1,4-naphthoquinones (in particular phosphobetaines) (Table 5) also may be inhibitors of cancer cell growth and efficient antioxidants protecting cells from mutagenesis, either spontaneous or induced by $H_2O_2$ [42].

Organoborates are widely used in various areas of chemistry. Their polyfluorinated analogues (Table 6) were used as initial reagents to synthesize the compounds of hypervalent bromine, iodine and xenon [43–45]. They are powerful tools to introduce polyfluorinated building blocks into organic molecules for the synthesis of a series of polyfluoraryltrifluoroborates with substituents other than fluorine atoms.

TABLE 5

Results of fluorine determination in organophosphorous compounds

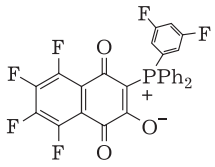
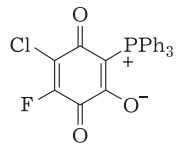
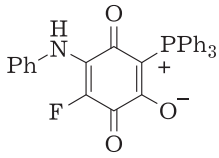
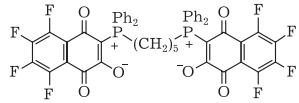
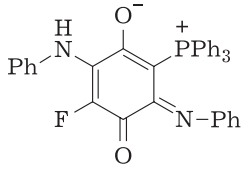
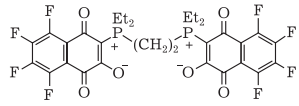
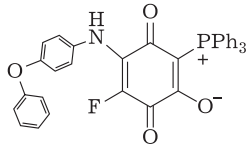
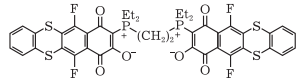
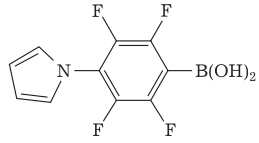
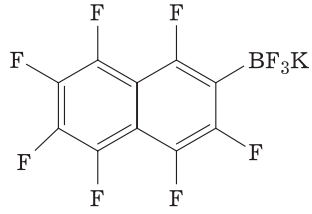
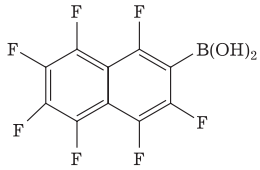
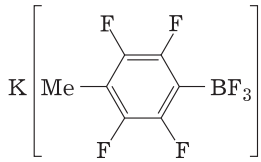
| Compound | Calculated according to the formula | Found | Compound | Calculated according to the formula | Found |
|---|---|---|---|---|---|
|  | 21.02 | 20.83 |  | 4.35 | 4.04 |
|  | 3.85 | 3.91 |  | 16.37 | 16.31 |
|  | 3.34 | 3.15 |  | 21.89 | 21.91 |
|  | 3.24 | 3.50 |  | 8.45 | 8.59 |

TABLE 6

Results of fluorine determination in perfluorinated organoborates and arylxenon(II) tetrafluoroborates

| Compound | Calculated according to the formula | Found | Compound | Calculated according to the formula | Found |
|---|---|---|---|---|---|
|  | 29.1 | 29.3 |  | 52.8 | 52.8 |
|  | 44.2 | 44.6 |  | 48.8 | 49.3 |
| $[C_6F_5Xe][BF_4]$ | 44.4 | 44.3 | $[2,3,4,5\text{-}C_6F_4HXe][BF_4]$ | 41.3 | 42.0 |

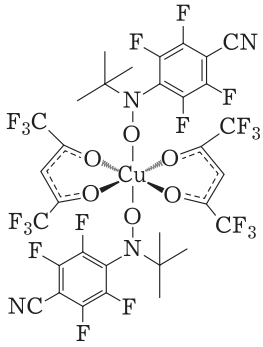
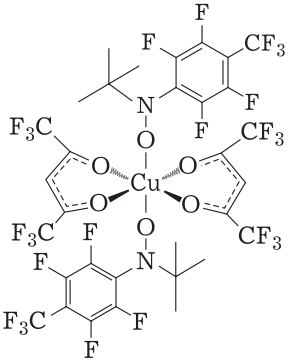
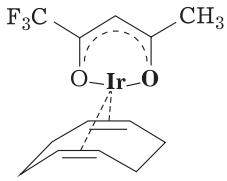
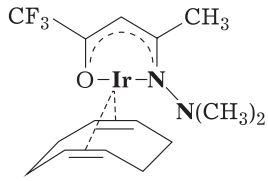
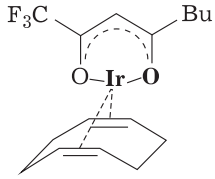
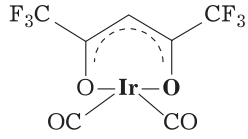
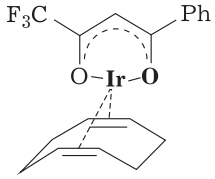
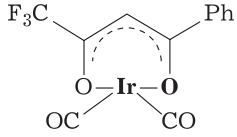
Results of fluorine determination in metal-containing organofluorine compounds are presented in Table 7.

Using a representative series of polyfluorophenylmercurials, the dependence of chemical shifts in NMR $^{199}Hg$ spectra and the constants of spin-spin interactions $J$ (Hg, F) on solvent, concentration, temperature and ligand nature was investigated [46].

The chemistry of organogermanium compounds is one of the oldest areas of the chemistry of organometallic compounds. Complete or nearly com-

TABLE 7

Results of fluorine determination in organometallic compounds

| Compound | Calculated according to the formula | Found | Compound | Calculated according to the formula | Found |
|---|---|---|---|---|---|
| | | | **Mercury** | | |
| $C_6F_5HgC_2H_5$ | 23.0 | 23.9 | 4-$CF_3C_6F_4HgOCOCF_3$ | 35.1 | 35.8 |
| 2,3,4,5-$C_6HF_4HgC_2H_5$ | 20.4 | 20.1 | $(2\text{-}C_{10}F_7)_2Hg$ | 33.0 | 37.6 |
| $(4\text{-}CF_3C_6F_4)_2Hg$ | 41.96 | 41.96 | 2-$C_{10}F_7HgCl$ | 27.2 | 27.1 |
| | | | **Germanium** | | |
| $(C_6F_5)_4Ge$ | 51.7 | 51.3 | $(C_6F_5)_2GeCl_2$ | 40.0 | 39.8 |
| $(C_6F_5)_2(C_6H_5)GeBr$ | 33.7 | 33.7 | $(C_6F_5)_2(C_6H_5)GeCl$ | 36.4 | 36.6 |
| | | | **Copper** | | |
|  | 38.00 | 38.11 |  | 45.48 | 45.44 |
| | | | **Iridium** | | |
|  | 12.6 | 12.2 |  | 11.5 | 11.5 |
|  | 11.5 | 11.6 |  | 24.8 | 25.0 |
|  | 11.1 | 11.0 |  | 12.3 | 12.5 |

plete replacement of hydrogen atoms by fluorine atoms in the organic groups at the germanium atom causes drastic qualitative differences in the properties of perfluorinated organogermanes in comparison with non-fluorinated initial compounds [47].

Organofluorine compounds with copper are ferromagnetics [48].

Volatile complex compounds of iridium are currently under intense investigation due to the possibility of using them as precursors for obtaining functional film materials based on iridium and its oxide $IrO_2$ by means of chemical vapour deposition. The advantages of this method include precise control of the composition and microstructure of the formed material, the possibility coating deposition onto the objects with complicated geometry (including structure with the high aspect ratio), deposition of refractory coatings (the melting point of iridium is 2466 °C) at relatively low temperature (200–800 °C). Protective, anticorrosion, buffer, optical, mechanical,

sensor and electrocatalytic properties of iridium-containing film materials determine the major areas of their application: aerospace technologies, catalysis, medicine, *etc.* [49–51].

Intercalation compounds of fluorographite (FGIC) [52] (Table 8) may be used as precursors for new catalysts and the new forms of expanded graphite (fluorographite), promising for electrochemical applications and for absorbers of electromagnetic radiation. The application of FGIC for obtaining so-called readily soluble graphite and conducting graphene layers was demonstrated. Treatment of FGIC surface with water vapour and electron beam leads to the formation of thin carbon graphene layers on the surface of the insulating substrate made of graphite fluoride. These materials are promising as gas sensors.

TABLE 8

Results of fluorine determination of the intercalation compounds of fluorographite

| Composition | % F* |
|---|---|
| $(C_2F_{0.76}Br_{0.01} \cdot 0.126CH_3CN)_n$ | 32.49 |
| $(C_2F_{0.66}Br_{0.01} \cdot 0.108CH_3CN)_n$ | 30.01 |
| $(C_2F_{0.35}Br_{0.026} \cdot 0.061CH_3CN)_n$ | 18.85 |
| $(C_2F_{0.25}Br_{0.036} \cdot 0.028CH_3CN)_n$ | 14.13 |
| $(C_2F_{1.05} \cdot 0.115Br_2)_n$ | 31.92 |

* Error of determination ±1.15 %.

## CONCLUSION

The procedure of fluorine determination proposed in the present work, based on decomposition of organic compounds in a flask filled with oxygen, and the formation of coloured fluoride complex with lanthanum alizarin complexone is universal, which is confirmed by its successful application for the analysis of various fluorine-containing objects:

– polyfluoroaromatic compounds containing fluorine up to 80 wt. %;

– polyfluoroaromatic substances containing other halogens in any combinations;

– polyfluorinated aromatic compounds containing sulphur in various functional groups;

– compounds of graphite and graphene, in particular those containing also other halogens;

– organoboron compounds;

– complexes with various metals.

The use of special additives allowed one to achieve complete decomposition of the organic substance avoiding the matrix influence on the results of analyses.

The applicability of this procedure for the purposes of elemental organic analysis is provided by the small error in fluorine determination, which does not exceed 0.5 abs. %.

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