

A Comprehensive Approach to Investigating Fluorine-Bearing Gas Mixtures

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Abstract

An integrated method is proposed for examining the compositions of fluorine-bearing gaseous mixtures, which allows for determining the concentration of HF, F₂, N₂, O₂, CO₂, CF₄, and C₂F₆ in these mixtures. The concentration of hydrogen fluoride is determined by its sorption on sodium fluoride followed by the determination of the fluoride ion by the potentiometric method. The lower threshold of determination of hydrogen fluoride is found to be 0.09 vol.%. The concentrations of N₂, O₂, CO₂, CF₄, and C₂F₆ are determined by the gas chromatographic method using a thermal conductivity detector. The proposed gas-chromatography method offers a quantitative measurement of the concentration of N₂, O₂, CO₂, CF₄, and C₂F₆ at the lower limits of detection of 0.008, 0.012, 0.011, 0.009, and 0.019 vol.%, respectively. Based on the developed method, the compositions of a standard fluorine-nitrogen (10 vol.%) and anodic gas samples, synthesized in a laboratory electrolyzer at the National Research Tomsk Polytechnic University and in an industrial electrochemical reactor at JSC Siberian Chemical Plant (Russia), are studied.

1. Introduction

Elemental fluorine is extensively applied in modern engineering: it is used in the production of uranium hexafluoride in a nuclear fuel cycle [1], carbon tetrafluoride [2] and nitrogen trifluoride [3, 4]; it is used for silicon etching in CVD processes, for the manufacture of a gas dielectric – sulfur hexafluoride, a variety of fluorinated carbon-bearing compounds [5–9] and other materials [10].

The only method of industrial production of fluorine is the fused electrolysis of KF·2HF in a steel electrochemical reactor with a carbon anode [11–13], where anhydrous hydrogen fluoride (AHF) is fed to the electrolyte [14]. Commonly, the anodic gas contains more than 90 vol.% of flu-

orine, and the main impurity (about 5–7 vol.%) is hydrogen fluoride. In addition, the anodic gas may contain nitrogen, oxygen, oxygen difluoride, carbon and sulfur fluorides, oxides and oxyfluorides, perfluoroalkanes, and silicon tetrafluoride.

For certain practical fluorine applications, the concentration of the above-listed impurities is quite critical. For instance, the concentration of carbon tetrafluoride in a semiconductor-grade nitrogen trifluoride in the modern microchip manufacturing processes must not exceed a few tens parts-per-million [15]. The concentration of carbon tetrafluoride T in nitrogen trifluoride is determined using the concentration of carbon tetrafluoride in the fluorine used in manufacturing nitrogen fluoride via fluorinating ammonium polyfluoride [4].

In the manufacture of carbon tetrafluoride, carbon polyfluoride and sulfur hexafluoride, the content of oxygen in fluorine is of great importance, since during fluorination of carbon and sulfur by

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oxygen-bearing fluorine the highly toxic carbon and sulfur oxyfluorides can be formed.

When fluorine is used as a lasing gas in excimer lasers, it is important to minimize the content of hydrogen fluoride and nitrogen in it [16].

During fluorination of organic compounds using fluorine: for instance, in the surface modification of polymers, the mixtures of fluorine with inert gases are used. Furthermore, hydrogen, contained in fluorine, can oxidize the fluorinated substance [17]. For these processes it is, therefore, important to determine the concentrations of nitrogen and oxygen in the mixtures with fluorine.

When high-purity fluorine is manufactured by cryogenic rectification, one has to know the content of perfluoroalkanes in it, such as hexafluoroethane, in order to rule out their accumulation in the rectification column cube, which can result in spontaneous ignition of perfluoroalkanes in fluorine. It is therefore important to study the compositions of the anodic gas, fluorine and its mixtures with inert gases.

At present, fluorine is analyzed using IR spectroscopy and mass spectrometry [18]. Nevertheless, no comprehensive method has been developed so far, which would allow determining the concentrations of most of the above-enumerated mixtures.

The purpose of this study is to develop an integrated method for the determination of the fluorine (anodic gas) composition and its mixtures with inert gases.

2. Experimental

The following methods were used for the determination of the compositions of fluorine-bearing mixtures:

- the concentration of hydrogen fluoride was measured by fixing it with sodium fluoride to form $\text{NaF}\cdot\text{HF}$ and then measured the fluoride ion in a water solution of $\text{NaF}\cdot\text{HF}$ using potentiometric titration;

- the concentration of fluorine was measured by determining the content of iodine liberated during the interaction of the fluorine-bearing mixture with potassium iodide;

- the concentration of N_2 , O_2 , CO_2 , CF_4 , and C_2F_6 was determined by gas chromatography using a thermal conductivity detector after removing hydrogen fluoride and fluorine from the mixture with sodium fluoride and potassium iodide, respectively.

The main concern in determining the fluorine content is its extremely high chemical reactivity.

For this reason, prior to the analysis the initial anodic gas samples were diluted with inert gases. The inert diluter was high-purity nitrogen. Nitrogen exhibits chemical inertness towards fluorine and its density is comparable with that of the latter; moreover, nitrogen is readily available commercially. In the case where it was necessary to monitor the content of nitrogen in fluorine, the dilution was performed using helium. After completing all of the analyses on the gas mixture composition, the results were recalculated with respect to the initial content of fluorine, using the dilution coefficient.

The gas mixtures were prepared on a setup preliminary surface-passivated with fluorine. A 10-liter stainless steel vessel, in which the gas mixtures were prepared, and all the gas lines were evacuated to a pressure of not higher than 20 mbar. The pressure in the system was determined using the MVP4A-Ks UHL1 IP63 fluorine-passivated pressure gages (OAO Manotom', Tomsk, Russia) with a pressure measuring range from minus 0.1 to 0.9 MPa and a D1 pressure gage of the ID-IV-CS-T IP65 trademark (OOO Point, Polatsk, Belarus) with a pressure measuring range from minus 0.1 to 0.8 MPa. Afterwards, anodic gas was delivered to the system from a 40 l-cylinder and, after the pressure had stabilized, the cylinder with the anodic gas was switched off from the system. Using the readings of the pressure gages, we determined the amount of the anodic gas supplied for mixing. The amounts of nitrogen and helium needed for achieving the target concentration were supplied to the system, monitoring the process in accordance with the readings of the pressure gages. The resulting mixtures were held for 12 h (in the case of nitrogen) and for 24 h (in the case of helium) for the mixture to homogenize, followed by a quantitative determination of the fluorine content. It has been experimentally found that the most appropriate fluorine concentration in the mixture for analytical testing is 10–25 vol.%.

The following compounds and substances were used in this study: sodium fluoride, potassium iodide, water-soluble modified starch indicator, sodium thiosulfate, sodium chloride, Trilon B, acetic acid, and sodium hydroxide – all of these were of chemical purity (OOO Khimmedsnab, Russia); state standard samples of O_2 (SSS 2.04±0.06 vol.%), N_2 (10.19±0.31 vol.%), CO_2 (5.16±0.15 vol.%) in helium (OOO Chistye gazy, Russia); fluorine gas mixture (10 vol.%) in nitrogen (OOO Fossen Em Ay I; State Standard Samples of fluoride ions in water (SSS 7261-96, OOO UZPH);

gaseous carbon tetrafluoride (OOO Horst); gaseous hexafluoroethane (OOO Horst); gaseous nitrogen (Grade A according to Specs. 6-21-39-96, Tomsk branch of OAO Avtogennyi zavod), gaseous helium (pressurized, Grade 5.0 Specs. 0271-001-45905715–2016, Tomsk branch of OAO Avtogennyi zavod); anodic gas was obtained from National Research Tomsk Polytechnic University (NR TPU) and JSC Siberian Chemical Plant (JSC SCP). All analyses used deionized water from an electroosmotic pump.

3. Results and discussion

3.1. Determination of hydrogen fluoride concentration

During the preparation of fluorine by an electrolytic process, hydrogen fluoride invariably enters the anodic gas. For certain fluorine applications, such as, for instance, laser engineering; the presence of HF is a very important parameter. Therefore, the determination of the HF concentration is an urgent task.

The essence of the detection method consists of the formation of a complex salt of hydrogen and sodium fluorides via the following equation:



It should be noted that at room temperature the equilibrium pressure of hydrogen fluoride vapors above $\text{NaF} \cdot \text{HF}$ is 0.4 Pa [19], which ensures the ratio of hydrogen fluoride by sodium fluoride at 25 °C close to 100% [20]. Therefore, using sodium fluoride one can nearly completely extract hydrogen fluoride from the anodic gas.

For the analysis, 10 g of sodium fluoride (exact weight) were placed into a fused silica absorption cartridge and flew a mixture of nitrogen and anodic gas was through it at a flow rate of 2 ml·s⁻¹. The characteristic size of sodium fluoride particles was about 100 μm and its humidity was ≈ 0.1%. The gas volume flow rate was set using a Bronkhorst gas flow controller of the LOW-ΔP-FLOW type. The flow time for the anodic gas and fluorine mixture through the cartridge was measured using a stop-watch timer. The mixture volume was calculated as a product the volume flowed rate by the time of the mixture flow through the cartridge. The content of the cartridge was quantitatively transferred into a plastic cup and diluted with 250 ml of distilled water. A 0.1 ml aliquot was sampled from the resulting solution, transferred to a 100 ml

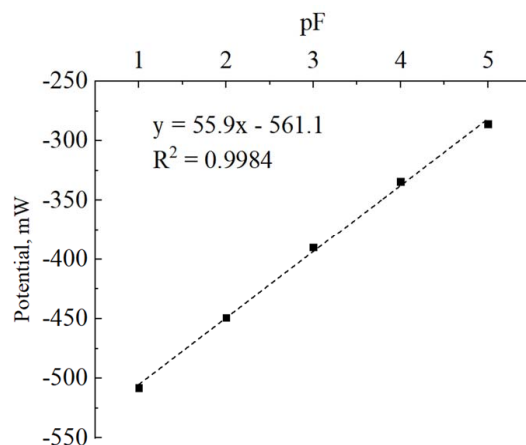


Fig. 1. Calibration curve of potentiometric determination of the fluorine ion content using a fluorine-selective electrode.

capacity measuring flask and added with water to make up the volume. The content of fluoride ion in the solution was determined by the potentiometric analysis using a fluorine-selective electrode [21]. The analytical system consisted of an Anion 4100 ionometer used in conjunction with an ELIS-131F fluorine-selective electrode and an ESr-10101 silver chloride reference electrode. The fluorine-selective electrode was calibrated in the range from 1 to 5 pF (Fig. 1). This calibration range offers a quantitative determination of the HF concentration from 0.09 to 10 vol.% in the anodic gas.

The content of hydrogen fluoride in the gas mixture was calculated using the following formula:

$$C_{\text{HF}} = \frac{10500C_{\text{F}} - m_{\text{NaF}}}{1.87G \cdot t} \cdot 1000 \cdot 100\%$$

where C_{HF} is the volume concentration of hydrogen fluoride in the anodic gas, %; C_{F} is the fluoride-ion concentration in the solution, mol·l⁻¹; m_{NaF} is the sodium fluoride mass; t is the time of the nitrogen and anodic gas flow through the absorbing cartridge, s; and G is the gas mixture volume flow rate, ml·s⁻¹.

The lower HF detection threshold was determined by a consecutive dilution of the fluorine-nitrogen mixture to a concentration where no increase in the fluoride ion concentration was observed. The lower detection threshold was found to be 0.09 vol.%.

The quantitative data on the content of hydrogen fluoride in the fluorine-nitrogen mixture from OOO Fossen Em Ay I and in the anodic gas samples obtained from NR TPU and JSC SCP are given in Table 1.

Table 1

Content of hydrogen fluoride in the anodic gas samples

Sample	Content of HF, vol. %
NR TPU	13.47
JSC SCP	5.89
OOO Fossen Em Ay I	≤ 0.09

The data listed in Table 1 suggest that the concentration of hydrogen fluoride in the anodic gas produced at JSC SCP is typical for the process of medium-temperature electrolysis. A high concentration of HF in the anodic gas synthesized at NR TPU is due to an increased (compared to the standard KF/HF ratio) content of hydrogen fluoride in the electrolyte. The fluorine-nitrogen mixture of OOO Fossen Em Ay I has been cleaned from hydrogen fluoride to a level of not higher than 0.1 vol.%.

3.2. Determination of fluorine concentration

The essence of the method consists of the substitution reaction between gaseous fluorine and potassium iodide to form metal iodine according to the following equation:



For the analysis, 10 g of potassium iodide powder were placed into the absorbing cartridge and flew the fluorine-nitrogen mixture through it at a flow rate of 2 ml·s⁻¹. The absorbing cartridge was a quartz tube with an inner diameter of 4 mm and a length of 25 cm. The assigned volume flow rate was sustained using a Bronkhorst gas flow controller of the LOW-ΔP-FLOW type, suitable for operations with fluorine-bearing gas mixtures. The time of the fluorine-nitrogen mixture flow through the cartridge was fixed by a stopwatch timer. Since the absorbing cartridge has a dead air volume, the time of the fluorine-nitrogen mixture flow was measured from the moment where the upper potassium iodide layer turned to yellow color (release of iodine). It was found out in this stage that for the process of fluorine absorption in the cartridge with potassium iodide to have a 'wavelike' character, we could observe a stepwise powder color change, in which case a white-to-yellow color transition occurs at a depth on the order of the size of the potassium iodide particle (about 100 μm), potassium iodide must exhibit a moisture content in the range from 0.1 to 0.2 wt.%. At lower moisture content, the

stepwise character of the powder color change gets degenerates, in the case of dry potassium iodide fluorine is not completely absorbed by the specified size of the absorbing cartridge at the volume flow rate used, and no darkening front is observed. It is well known that fluorine reacts with water to form oxygen and hydrogen fluoride. Hydrogen fluoride and oxygen are swept off from the system without interacting with KI. The amount of fluorine spent on its interaction with water is as low as about 2%; this value can be neglected in further calculations of the fluorine-nitrogen mixture composition.

The volume of the fluorine-nitrogen mixture was calculated as a product of the volume flow rate by the time the mixture flowed through the cartridge. The content of the cartridge was quantitatively transferred to a glass cup and diluted with 30 ml of deionized water. The solution of iodine was titrated using a 0.1 H solution of sodium thiosulfate according to GOST 25699.3-90 [22].

The volume concentration of fluorine in the fluorine-nitrogen mixture was calculated using the following formula:

$$C_F = \frac{V_t \cdot C_t \cdot 11.2}{t \cdot G} \cdot 100\%$$

where C_F is the volume concentration of fluorine in the gas mixture, %; V_t is the volume of the sodium thiosulfate solution, ml; C_t is the mole concentration of sodium thiosulfate, mol·l⁻¹; t is the time of the fluorine-nitrogen mixture flow through the absorbing cartridge, s; and G is the volume flow rate of the fluorine-nitrogen mixture, ml·s⁻¹.

Table 2 presents the measured concentrations of fluorine, preliminary cleaned from hydrogen fluoride by sodium fluoride, in its mixture with nitrogen, which were obtained by a procedure using potassium iodide and by the barometric method.

Table 2

Quantitative determination of fluorine in the fluorine-nitrogen mixture

Sample origin	Content of fluorine determined by the barometric method, %	Content of fluorine determined by the titration method, %
OOO Fossen Em Ay I	—*	10.11
JSC SCP	10.23	10.17
NR TPU	10.09	9.93
*Not measured		

The results obtained prompt a conclusion that the barometric and titration methods demonstrate similar data, the difference being not more than 0.2%. Note that the concentration values obtained by the titration method are lower than the results obtained from the pressure measurements.

3.3. Determination of the concentrations of nitrogen, oxygen, carbon dioxide, carbon tetrafluoride and hexafluoroethane

The main impurities in fluorine are N_2 , O_2 , CO_2 , CF_4 , and C_2F_6 . Nitrogen is present due to its use in purging the process equipment. The presence of oxygen is caused by water in the electrolyte, which is supplied together with hydrogen fluoride. Carbon dioxide is the product of the carbon anode oxidation by oxygen, carbon tetrafluoride and hexafluoroethane are the anode fluorination products.

In order to monitor the above-enumerated components, we used the method of gas chromatography.

Simultaneous separation of this mixture is a nontrivial problem for analytical chemistry. Oxygen and nitrogen are separated in selective chromatographic columns at low temperatures, which under the conditions of this study would lead to long values of the retention time of perfluorinated alkanes. In this context, in order to develop an appropriate analytical technique, we used a simultaneous analysis of the gas mixture in two parallel columns with different immobile phases, accompanied by their detection using thermal conductivity detectors (TCDs).

For the analysis of oxygen and nitrogen we chose a NaX (3 m × 3 mm) column and for the separation and determination of the other gas mixture components we used an Agilent HayeSep Q (3 m × 3 mm) column. The technique was developed using a Kristall 4000M gas chromatograph equipped with two thermal conductivity detectors and a ten-way gas sampling valve. A peculiar feature of this configuration is the possibility of introducing a gas sample via the sampling valve simultaneously to both columns, followed by its detection in two independent TCDs, which is quite appropriate for this task.

After optimization of the separation technique, we identified the most reasonable conditions for the analysis. Helium was used as a carrier gas, its flow rate was $20 \text{ ml} \cdot \text{min}^{-1}$, and the detector temperature was $180 \text{ }^\circ\text{C}$. The process of separation was carried out in the following thermal regime:

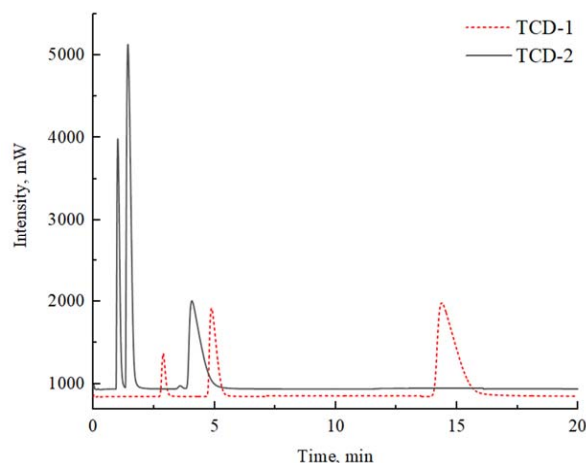


Fig. 2. Chromatogram of the gas mixture separation: on the NaX (3 m × 3 mm) column – TCD-1 and Agilent HayeSep Q (3 m × 3 mm) column – TCD-2.

$35 \text{ }^\circ\text{C}$ for 4 min, then heating to $90 \text{ }^\circ\text{C}$ at a rate of $10 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$, then exposure for 7 min at $90 \text{ }^\circ\text{C}$.

This method allowed us to obtain a high resolution of all of the mixture components and to achieve an optimal analysis time. Figure 2 presents the mixture chromatogram.

Thermal conductivity detector-1 is connected to the NaX column (3 m × 3 mm). This column was used for the determination of the concentration of nitrogen and oxygen in the gas mixtures. There are three well-resolved peaks in the chromatogram (Fig. 2): oxygen (retention time 2.88 min), nitrogen (retention time 4.87 min) and carbon tetrafluoride (retention time 14.37 min). The peaks from nitrogen and oxygen in this method are symmetrical and completely resolved, which gives a possibility of performing a quantitative analysis of these components.

Thermal conductivity detector-2 is connected to the Agilent HayeSep Q (3 m × 3 mm) column. There are four peaks in the chromatogram: co-elution nitrogen and oxygen (retention time 1.01 min), carbon tetrafluoride (retention time 1.42 min), carbon dioxide (retention time 3.58 min) and hexafluoroethane (retention time 4.06 min). Good resolutions of the peaks indicate the possible quantitative determination of the content of carbon tetrafluoride, carbon dioxide and hexafluoroethane.

To elaborate on the method of quantitative analysis, the chromatograph was calibrated using the above described procedure. To do so, a number of standard gas mixtures were analyzed using injection loops of different volumes (1, 0.5, 0.25 and 0.125 ml); the analyses were repeated three times and the series-average values were in the calcula-

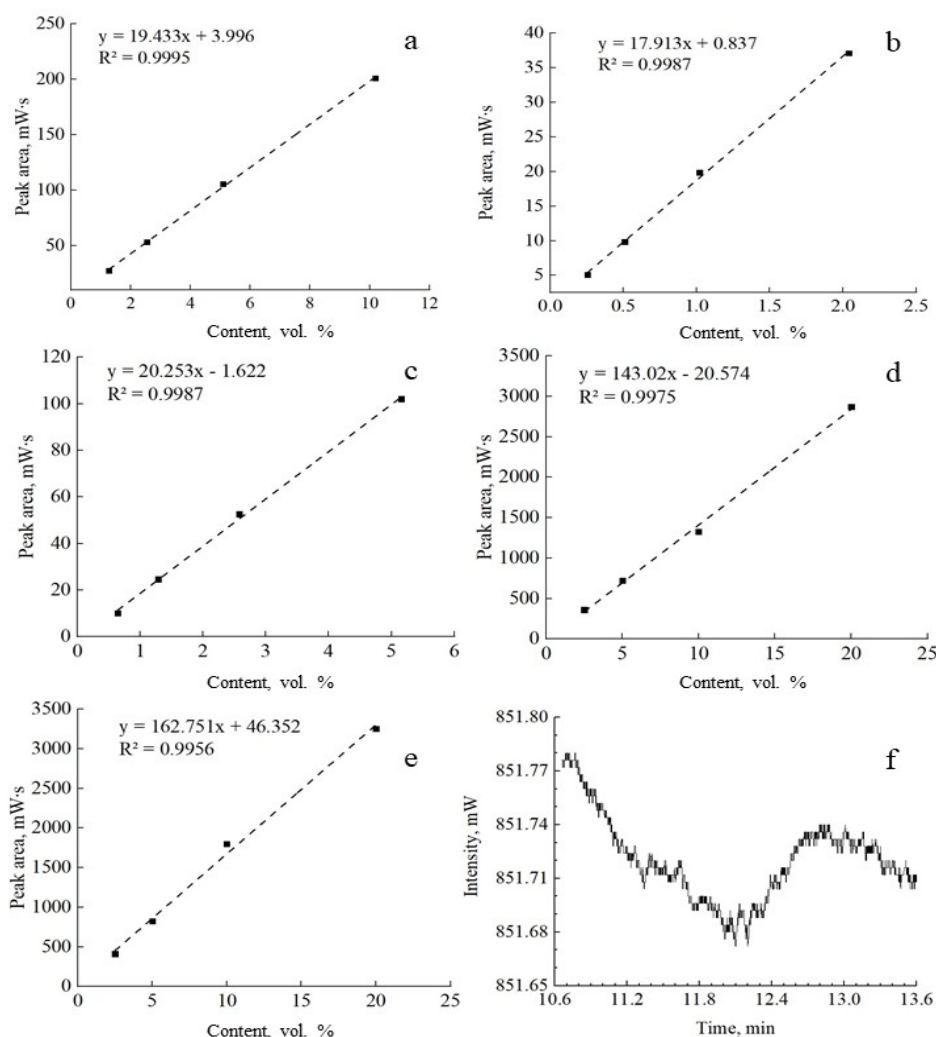


Fig. 3. Calibration curves for quantitative determination of N_2 (a), O_2 (b), CO_2 (c), CF_4 (d), C_2F_6 (e) and noise signal of the chromatograph baseline (f).

tions. Prior to the analysis, a blank test was performed; its results were subtracted from the results of the gas mixture analyses. The resulting data concerning the peak area dependence on the concentrations are given in Fig. 3.

The coefficients of the linear regression correlation of the calibration curves are more than 0.99, which indicates a linear dependence in the selected ranges. In addition, the values of b in the regression equations are smaller than 2% of the target peak area value, which suggests a small error in the method.

Of no minor importance is the problem of analytical determination of the lower limit of quantification (LLOQ) and lower limit of detection (LLD) of the components. The lower levels were calculated using the signal-noise (S/N) ratios; for LLOQ, it was taken to be $S/N = 3$, and for LLD $S/N = 10$. Figure 3 gives the baseline noise, and Table 3 presents the components' values of LLOQ and LLD.

Table 3
LLOQ and LLD for the gas mixture components

Analyte	LLD, %	LLOQ, %
O_2	0.002	0.008
N_2	0.003	0.012
CO_2	0.003	0.011
CF_4	0.003	0.009
C_2F_6	0.006	0.019

When analyzing a fluorine-bearing gas mixture, it is impermissible to let fluorine and hydrogen fluoride into the analytical equipment. To rule out their contact with the equipment, before the chromatographic analysis the fluorine-bearing mixture was passed through a cartridge with sodium fluoride in order to remove hydrogen fluoride and then through a cartridge with potassium iodide to remove fluorine. The moisture content in potassium iodide was monitored and maintained in the range from 0.1 to 0.2%.

Table 4

Concentrations of oxygen, carbon dioxide, carbon tetrafluoride and hexafluoroethane in a 10% fluorine-nitrogen mixture from OOO Fossen Em Ay I and in fluorine from NR TPU and JSC SCP after removing hydrogen fluoride

Sample	Content of components, vol. %				
	O ₂	N ₂	CO ₂	CF ₄	C ₂ F ₆
NR TPU	0.34	0.78	0.36	0.014	≤ 0.019
JSC SCP	0.24	0.12	0.09	0.009	≤ 0.019
OOO Fossen Em Ay I	0.024	0.01	≤ 0.011	≤ 0.009	≤ 0.019

The integrated method for examination of the compositions of fluorine and its gas mixtures was tested using a 10% fluorine and nitrogen mixture manufactured by OOO Fossen Em Ay I and 10% fluorine obtained from NR TPU and JSC SCP in the mixtures with nitrogen and helium. Table 4 presents the concentrations of oxygen, nitrogen, carbon dioxide, carbon tetrafluoride and hexafluoroethane in the mixture from OOO Fossen Em Ay I and in fluorine from NR TPU and JSC SCP after hydrogen fluoride was removed from it by sodium fluoride.

The results presented in Table 4 imply that no hexafluoroethane has been detected in any of the tested mixtures; the content of carbon tetrafluoride in the fluorine sample from JSC SCP is 90 ppm and in the fluorine sample from NR TPU – 140 ppm; the content of oxygen, nitrogen and carbon dioxide in the fluorine samples from JSC SCP and NR TPU is about 10⁻¹ vol.%. Such a high content of impurities in the fluorine sample from NR TPU is likely to be due to periodic start-ups of the electrolyzer, while at JSC SCP the electrolysis occurs in a continuous mode.

4. Conclusions

In this study, we have developed an integrated method for the examination of the compositions of fluorine-bearing mixtures formed by mixing the anodic gas in the electrolysis plants with nitrogen.

The concentration of hydrogen fluoride was measured by a potentiometric technique by analyzing the solution of sodium bifluoride produced during the processing of sodium fluoride with the anodic gas (or its mixtures with inert gases) at room temperature. This method allows determining the content of hydrogen fluoride in the anodic gas in the concentration range from 0.1 to 10 vol.%.

The concentration of fluorine in its mixtures with inert gases was determined by fixing fluorine with potassium iodide, followed by titration of the

released iodine after removing hydrogen fluoride from the gas mixture by iodine using sodium fluoride.

The concentrations of nitrogen, oxygen, carbon dioxide, carbon tetrafluoride, and hexafluoroethane were determined chromatographically after removing hydrogen fluoride from the mixtures with sodium fluoride and removing fluorine with potassium iodide. The LLOQ values for the gases were as follows: 0.008% (O₂), 0.012% (N₂), 0.011% (CO₂), 0.009% (CF₄), and 0.019% (C₂F₆).

Using the proposed method, we examined the anodic gas compositions synthesized in a laboratory electrolyzer of NR TPU and the composition of the samples manufactured at JSC SCP, as well as that of the fluorine-nitrogen mixture from OOO Fossen Em Ay I. The anodic gas composition from AO SCC is as follows: 0.24% (O₂), 0.12% (N₂), 0.09% (CO₂), 0.008% (CF₄). The anodic gas composition from NR TPU is as follows: 0.34% (O₂), 0.78% (N₂), 0.36% (CO₂), 0.014% (CF₄). Hexafluoroethane was not detected in the samples from NR TPU or JSC SCP.

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