

DETERMINATION OF IODIDES AND BROMIDES IN ASSOCIATED PRODUCED GROUNDWATER BY THE VISUAL TEST METHOD

NATALIIA NIKITINA ¹, OLENA RESHETNYAK¹, NATALIA NEMETS², OKSANA CHERNYSHOVA³, POLINA LUKOVYKOVA¹

¹Kharkov V.N. Karazin National University, Svoboda sq., 4, Kharkov 61022, Ukraine; e-mail: nikitina@karazin.ua

²JSC UkrGasvydobuvannya, Kudriavska str., 26/28, Kyiv 04053, Ukraine

³State Scientific Institution “Institute for Single Crystals” of National Academy of Sciences of Ukraine, Nauki Ave., 60, Kharkov 61072, Ukraine

 Corresponding author

Received: 31 May 2025 / **Accepted:** 30 November 2025

Abstract

Nikitina N., Reshetnyak O., Nemets N., Chernyshova O., Lukovkyova P.: Determination of iodides and bromides in associated produced groundwater by the visual test method. *Ekológia (Bratislava)*, Vol. 45, No. 1, p. 1–7, 2026.

A technique has been developed for the semiquantitative visual determination of iodide and bromide ions in their simultaneous presence in highly mineralized produced waters from oil and gas condensate fields. The technique is based on the oxidation of iodine to iodide with potassium iodate and bromide to bromine with potassium bromate, followed by the bromination of fluorescein with the formation of eosin. Both iodine and eosin were adsorbed by modified polyurethane foam tablets. The conditions for visual determination of the indicated analytical forms were investigated. The limit of quantification using the color scale was 3.2 mg/L for bromide ions and was 0.48 mg/L for iodide ions. The determination range was 5–80 mg/L for Br[−] contents and 0.5–16 mg/L for I[−]. The semiquantitative method with visual detection is expressed and suitable for the analysis of associated produced groundwater: the analysis time is reduced threefold compared to the quantitative determination method using oxidation–reduction titration.

Key words: iodide, bromide, produced water, color scale, polyurethane foam, visual determination, eosin.

Introduction

Associated produced waters (APWs) are waters that rise to the surface together with oil and gas during their extraction and, after settling, are returned to deep horizons of oil and gas fields. The waters are classified as highly mineralized by their composition and contain a significant amount of dissolved chemical elements and compounds. Information about the general nature of mineralization of APW and the content of individual specific components, which include iodine and bromine, is very important for the search and exploration of oil and gas fields. Elements I and Br, 90–95% of which are present in groundwater in the form of I[−] and Br[−] anions, have high mobility and form extensive dispersion halos; they are classified as hydrogeochemical indicators of hydrocarbon deposits and oil and gas accumulations. At the depth of 3000–5000 m, the mass concentration of iodine in APW in the eastern region of Ukraine reaches 100 mg/L, while bromine reaches 1000 mg/L; the bromine content is 10–150 times higher than the iodine content.

Associated produced groundwater can be a raw material for obtaining iodine and bromine, which are in short supply worldwide. It is known that the minimum content of I and Br for their cost-effective mining is 18 and 250 mg/L, respectively. Currently, methods for extracting I[−] and Br[−] anions from aqueous media

using the ion exchange method have been developed (Sanemasa et al., 2008), and methods for obtaining molecular iodine by treating APW with oxidizing agents, Cl₂, NaClO, SO₃, H₂O₂, or O₃, have been proposed.

The technology of APW ozonation without adding strong acids and catalysts is more environmentally friendly (Niemets et al., 2019).

Preliminary data on the halide content are necessary for the development and optimization of extraction technological processes and for the timely detection of pollution. For analyzing water bodies containing iodides and bromides, various methods have been used: ion chromatography with various methods of postcolumn detection (Buchberger, 1988; Eickhorst et al., 2004; Cheng et al., 2005; Mehra, Frankenberger, 1990), gas chromatography (Reddy-Noone et al., 2007), luminescence spectroscopy (Zhu et al., 1990; Fu et al., 2017; Pilipenko et al., 1989; García-Figueroa et al., 2017), surface plasmon resonance method (Bothra et al., 2015; Liu et al., 2023), spectrophotometry (Dobolyi, 1984; Fukushima, Aikawa, 2021; Amourizi et al., 2020; Zhang et al., 2000), capillary isotachopheresis (Fukushi, Hiroy, 1997), amperometry, and potentiometry (De Souza et al., 2016). The methods are characterized by different selectivity and different values of quantification limit (LOQ): for iodides from 3·10^{−6} mg/L (Pilipenko et al., 1989) to 5 mg/L (Cheng et al., 2005) and for

bromides from $1.3 \cdot 10^{-6}$ mg/L (Pilipenko et al., 1989) to 5 mg/L (Cheng et al., 2005).

The use of hybrid analytical methods, including the extraction and concentration of analytes on sorbents with their subsequent determination in the sorbent phase, allows for the expansion of the list of analyzable objects and simplifies sample preparation. Different materials were used as sorbents for analytical control of iodides and bromides: paper (Zhu et al., 1990; Loh et al., 2015; Gorbunova et al., 2019), polymer films (Geddes, 2000), methylmethacrylate matrices (Fedan et al., 2018), membrane filters (Zuy, Maznzya, 2014), and polyurethane foams (PUF) (Trohimenko, Zaporozhets, 2014). Thin-film polymer sensors were used for the determination of I^- , Br^- , and Cl^- in weakly alkaline waters. The operating principle was in quenching the fluorescence of acridine fluorophore dyes covalently grafted to a hydrophilic copolymer. The films swelled in an aqueous medium, which facilitated the diffusion of halide ions and electrostatic interaction with the polymer cations of the dyes (Geddes, 2000). The operation of a fiber optic sensor, which allows the simultaneous determination of I^- ($c_{lim} = 3.8$ mg/L) and Br^- ($c_{lim} = 32$ mg/L) (Zhu et al., 1990), is based on the quenching of fluorescence of two fluorophores (quinine and harman) immobilized on paper.

Triacetylcellulose membranes with immobilized methyltriethylammonium chloride (Rastegarzadeh et al., 2009) and paper test strips modified with silver triangular nanoparticles (Gorbunova et al., 2019) were used to determine iodides in food products and mineral waters. The authors note that other ions, primarily Br^- and Cl^- , interfered with the determination.

A significant part of spectrophotometric and hybrid methods of determining I^- and Br^- is based on their oxidation to molecular forms and subsequent bromination of organic reagents. Chloramine T, KIO_3 , $KBrO_3$, KNO_2 , and oxone (potassium peroxomonosulfate) are most often used as oxidizing agents.

In the study by Zuy and Maznzya (2014), bromides were oxidized to bromine using sodium hypochlorite. The bromine then reacted with fluorescein in an acidified sample of natural water to form eosin. The addition of a cationic surfactant led to the formation of an ionic associate with a colored product; the solution was filtered through a nitrocellulose membrane filter, and the brightness of the colorimetric characteristics of the concentrates was measured. The determination of 50 $\mu\text{g/L}$ bromides was not interfered with by 1000-fold excesses of chlorides but was interfered with by equal amounts of iodides. A paper-based microfluidic analytical device was proposed for the colorimetric determination of bromides in produced waters (Loh et al., 2015). Three layers of Whatman filter paper were soaked in solutions of a pH 4.6 buffer, phenol red dye, and chloramine T. The color of the bottom layer of the paper surface changed from yellow to blue as a result of the dye bromination. RGB color characteristics were measured using a spectrophotometer or a wireless colorimetric sensor connected to a smartphone. LOQ of bromides was 3.2 mg/L; high concentrations of I^- and Cl^- did not significantly affect the results. Iodometric control of iodates in food salt was carried out by solid-phase spectrophotometry using optically transparent polymethacrylate matrices (Fedan et al., 2018). As a result of the interaction of iodate with excess iodide in an acidic medium, molecular iodine was formed, which was extracted into colorless polymer matrices.

A convenient and accessible sorbent for extraction, separation, and concentration of various inorganic and organic sub-

stances from aqueous media is polyurethane foam (PUF). This is a polymer based on simple or complex ethers; it is a multifunctional sorbent, has a membrane-cellular structure and high sorption capacity, and is not subject to decomposition as a result of chemical interactions. In 1970, Bowen H.J.M. proposed using polyurethane foam as a selective absorber for a range of substances, including molecular iodine (Bowen, 1970). For physical immobilization of organic and inorganic reagents or their extraction from aqueous solutions, polyurethane foams based on simple ethers are most often used (Bowen, 1970; Dmitrienko et al., 2002). Trohimenko and Zaporozhets (2014) proposed a method for solid-phase spectrophotometric determination of the total iodine content in samples with an organic matrix (dry milk, sunflower oil with certified iodine content). The method included the sorption of molecular I_2 on PUF, formed during the oxidation of iodide with oxone. They confirmed that PUF based on simple ethers has better characteristics for I_2 sorption, namely, higher values of the analytical signal, color stability of the modified sorbent, and, consequently, stability of the analytical signal over time.

It should be noted that the listed instrumental methods and techniques of chemical analysis are provided for single-component or total determination of halides. The standard method for monitoring the content of I^- and Br^- anions simultaneously present in APW in the gas production industry of Ukraine is the method of iodometric oxidation–reduction titration. The process is multistage and labor-intensive and requires the use of a large number of reagents, so there is a need for simpler and more selective analysis procedures.

The aim of this work was to study the possibility of semi-quantitative visual determination of iodides and bromides in samples of APW from oil and gas condensate fields using polyurethane foam as a sorbent.

Material and methods

All the solutions were prepared in distilled water using reagents qualified no lower than “analytical grade.” The initial solution of $5 \cdot 10^{-3}$ mol/L fluorescein was prepared by dissolving a weighed portion of the reagent in 96% ethyl alcohol. The required pH values in the solutions were created by adding sulfuric acid or an acetate buffer solution.

PPU tablets with a diameter of 16 mm, a height of 10 mm, and a weight of ~ 0.03 g were made from sheet polyurethane foam based on mixed ether. The tablets were cleaned by keeping them in a 0.1 mol/L H_2SO_4 solution for 30 min, then washed successively with distilled water to pH 4–5, followed by acetone, and dried in air.

Observation of the modified polyurethane foam tablets coloration was carried out on a white background under diffused lighting conditions (500–600 lux): polyurethane foam tablets were placed on a white sheet of paper, and the observer's eyes were at a distance of 40–45 cm.

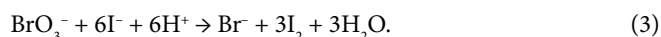
The diffuse reflection (R) of colored PUF tablets was measured on an SF-2000 spectrophotometer (St. Petersburg) with reference to blank samples. The measurement error for R did not exceed $\pm 0.5\%$. The obtained diffuse reflection values were recalculated into the Gurevich–Kubelka–Munk function (F) using the equation: $F = (1-R)^2/2R$.

The light absorption of the solutions was recorded on a Hitachi U-2000 spectrophotometer.

To confirm the accuracy of the results of determining iodides and bromides in their joint presence by the method proposed in this work, the well-known oxidation–reduction titration was used (Reznikov et al., 1970): after measuring the density of the sample of water being analyzed, the required volume of saturated potassium hypochlorite solution was added and boiled in a water bath for 10 minutes. Then, 10 mL of saturated boric acid solution was added to maintain pH 9, and boiling was continued for another 7 minutes. A 20% sodium formate solution was added to the hot solution to remove excess hypochlorite and boiled for 5 minutes. The reaction was monitored using iodine-starch paper. The hot solution was filtered. The iodate formed in the solution was titrated as follows: a 0.1% solution of methyl orange and a 2 mol/L solution of sulfuric acid were added until a bright pink color appeared. After cooling the sample, 5 mL of a 20% solution of potassium iodide was added, and the released iodine was titrated with a 0.01 mol/L solution of sodium thiosulfate until the color of the solution changed to light yellow. A few drops of starch were added, and titration was continued until the solution became colorless. At the same time, the following reactions occurred in the solution:



After the titration was completed, 10 mL of 25% sulfuric acid solution and a few drops of 1% ammonium molybdate solution were added to the same sample to speed up the reaction between bromate and iodide. The flask was closed with a stopper and kept in a dark place for 15 minutes to allow the bromate to interact with iodide:



The released iodine was titrated with a 0.1 mol/L sodium thiosulfate solution.

The mass concentrations of halides were calculated using the formulas:

$$c(\text{I}^-) = \frac{c(\text{S}_2\text{O}_3^{2-}) \cdot V(\text{S}_2\text{O}_3^{2-}) \cdot M(\text{I}^-) \cdot 1000}{V_{\text{sample}} \cdot 6}, \quad (4)$$

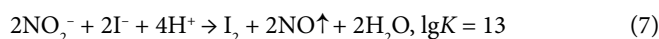
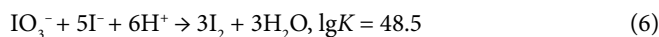
$$c(\text{Br}^-) = \frac{c(\text{S}_2\text{O}_3^{2-}) \cdot V(\text{S}_2\text{O}_3^{2-}) \cdot M(\text{Br}^-) \cdot 1000}{V_{\text{sample}} \cdot 6}, \quad (5)$$

where $c(\text{S}_2\text{O}_3^{2-})$ and $V(\text{S}_2\text{O}_3^{2-})$ are the molar concentration and volume of sodium thiosulfate solution used for titration (mL); $M(\text{I}^-)$ and $M(\text{Br}^-)$ are the molar masses of iodide and bromide ions, respectively; and V_{sample} is the volume of sample taken for titration (mL).

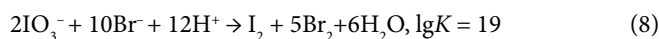
Results

Determination of iodide ions

The reactions of iodide ions oxidation (6, 7) were considered as test reactions for the determination of iodide ions. The reactions occur with the formation of molecular iodine, followed by the sorption by PUF tablets.



The effect of bromide ions would be less noticeable ($\lg K$ (equation 9) < $\lg K$ (equation 8)) in a case of using sodium nitrite as an oxidizer. But it was not used because of the interaction of the toluidine groups of PUF with NO_2^- – in an acidic medium. As a result the PUF tablets become yellow in the absence of molecular iodine.



In the case of using potassium iodate, such an effect was not observed, and a noticeable effect of bromide ions oxidation by iodate was observed only with a 100-fold excess of bromides.

The concentration of potassium iodate of 0.01 mol/L was chosen based on the data obtained by measuring the diffuse reflectance of polyurethane foam tablets after the contact of purified tablets with 25 mL of solutions of 0.1, 0.05, 0.01, $5 \cdot 10^{-3}$, $1 \cdot 10^{-3}$, and $5 \cdot 10^{-4}$ mol/L potassium iodate for 20 minutes. Each solution contained potassium iodide with a concentration of 15 mg/L, and pH 2 in each solution was created by adding sulfuric acid (Fig. 1).

The maximum of the Gurevich–Kubelka–Munk function for molecular iodine sorbed on PUF corresponded to 380 nm (Fig. 2(1)). It is noted in publications that the absorption spectrum of molecular iodine sorbed on PUF can have a maximum at 360 nm (Trohimenko, Zaporozhets, 2014) or 380 nm (Trohimenko, Zaporozhets, 2012) for PUF based on ethers; in the polymethacrylate matrix, the maximum of iodine absorption corresponds to 365 nm (Fedan et al., 2018).

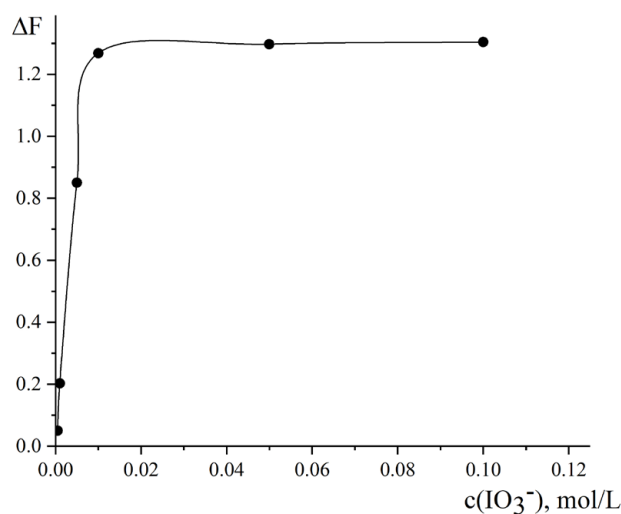


Fig. 1. Dependence of the Gurevich–Kubelka–Munk function on the concentration of potassium iodate.

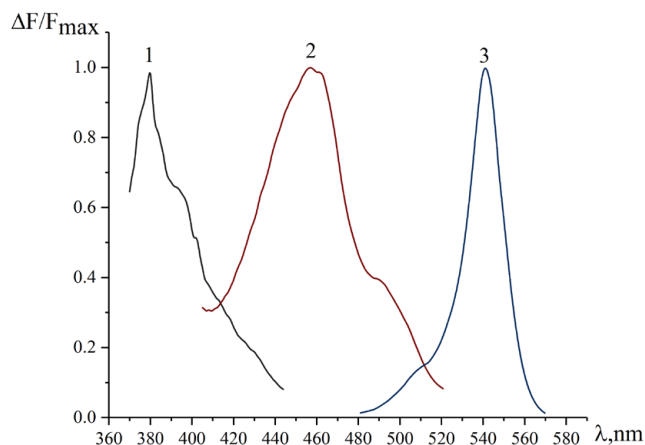


Fig. 2. Dependence of the normalized Gurevich–Kubelka–Munk function on the wavelength for PUF tablets with: 1, immobilized I_2 at $c(KIO_3)=0.01$ mol/L, $c(H_2SO_4)=0.01$ mol/L, $c(I^-)=4$ mg/L; 2, fluorescein at $5 \cdot 10^{-5}$ mol fluorescein/g PUF; 3, the product of fluorescein bromination reaction—eosin at $c(KBrO_3)=5 \cdot 10^{-3}$ mol/L, $c(H_2SO_4)=0.01$ mol/L, $c(Br^-)=40$ mg/L, $5 \cdot 10^{-5}$ mol fluorescein/g PUF.

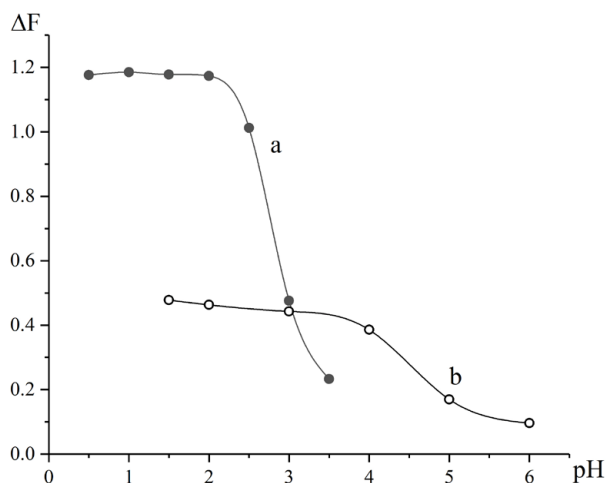


Fig. 3. Dependence of the Gurevich–Kubelka–Munk function on the pH of solutions: (a) sorption of molecular iodine from a solution containing 0.01 mol/L KIO_3 , 8 mg/L iodide ions, $\lambda_{max}=380$ nm; (b) sorption of fluorescein from a solution containing $5 \cdot 10^{-5}$ mol/L fluorescein, $\lambda_{max}=457$ nm.

Table 1. Results of the experimental evaluation of the visual limit of quantification (LOQ) of I^- visual determination using a color scale.

Iodide added, $c_{set}=1.0$ mg/L	Iodide found, using a color scale, mg/L (n=45)		
	0.6	0.9	1.2
The number of observations	2	28	15
$s_c = 0.16$ mg/L; LOQ = $3s_c = 0.48$ mg/L			

To choose the optimal value of the medium acidity, the diffuse reflection of the PUF tablets with sorbed molecular iodine was measured, varying the pH from 0.5 to 3.5. Each solution contained potassium iodate 0.01 mol/L and iodide with the concentration of 8 mg/L. Based on the obtained dependence (Fig. 3a), in further work, pH 2 was created in solutions by adding sulfuric acid.

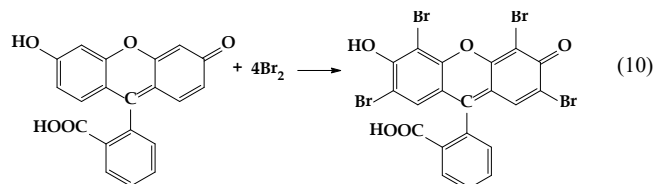
While studying the dependence of the Gurevich–Kubelka–Munk function on the time of sorption of molecular iodine by PUF tablets (Fig. 4a), the sufficient time for carrying out the test reaction, which was 20 minutes, was determined. In addition to the sorption time, the concentration of iodide also varied from 0.5 to 16 mg/L. Each solution contained potassium iodate and sulfuric acid with concentrations of 0.01 mol/L. The color of polyurethane foam tablets with immobilized iodine linearly depends on the concentration of iodide ions in the solution in the range of 0.5–16 mg/L and is described by the equation of the calibration function: $\Delta F = (0.164 \pm 0.014) \cdot c$ ($R^2=0.997$).

The estimation of the visual limit of quantification (LOQ) of I^- was carried out according to the algorithm developed by our team earlier: near the reference value of LOQ, in a narrow range of I^- concentrations, a color scale was prepared corresponding to the I^- content in a solution of 0, 0.6, 1.2 mg/L and a control solution with a concentration of $c_{set}=1.0$ mg/L. Fifteen independent observers estimated the I^- content of the control solution, with one of three possible answers available: the I^- concentration corresponds to the upper, lower, or middle value of the scale range. The experiment was repeated three times. Out of 45 test results, the values of the standard deviation of the desired concentration (s_c) and the value of LOQ were calculated, and the results are presented in Table 1.

The scale prepared for test determinations was stable for the next day. A gradual decrease in the tablet color intensity was observed, but not more than 5% relative to the initial intensity over 5 days, with the most noticeable evaporation of iodine being for high concentrations of iodide.

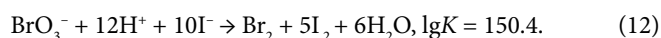
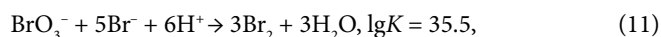
Determination of bromide ions

For bromide ions determination, the bromination reaction of fluorescein (10) was chosen, and potassium bromate with a molar concentration of $5 \cdot 10^{-3}$ mol/L was chosen as an oxidizing agent. García-Figueroa et al. (2017) proposed a method for determining bromide ions in waters after their oxidation with potassium bromate based on the results of measuring the fluorescence of tetrabromofluorescein; the reaction was carried out in the presence of 0.01 mol/L of sulfuric acid.



The task was to determine iodide and bromide ions in their joint presence. Therefore, to eliminate the interfering effect of iodide ions, they were first converted into molecular iodine by reaction with iodate (Eq. 6). After its quantitative determination, iodine was completely removed from the APW sample solution, since, with an iodide ion content of more than 5 mg/L, it inter-

feres with the determination of bromides (compare $\lg K$ Eq. 11, 12) during oxidation with bromate:



To completely remove I_2 from the solution, 20 minutes of sorption of the latter by two purified PUF tablets weighing 0.025 g is sufficient.

The optimal concentration of fluorescein, $5 \cdot 10^{-5}$ mol/L, for modifying PUF tablets, was chosen based on a study of the dependence of the Gurevich–Kubelka–Munk function on the concentration of fluorescein (Fig. 5).

The absorption maxima of fluorescein sorbed by PUF tablets (Fig. 2(2)) and in a 5% alcohol solution coincide and correspond to 457 nm. Based on the dependence of the Gurevich–Kubelka–Munk function on the pH of the solutions (Fig. 3b), a pH value of 2 was chosen for modifying the tablets, which was created with a solution of 0.01 mol/L sulfuric acid.

The time of the PUF tablets modification with a fluorescein solution was selected based on a study of the amount of fluorescein sorbed by one PUF tablet (X , mol/g) according to the results of measuring the light absorption of $5 \cdot 10^{-5}$ mol/L fluorescein solutions before and after the contact with purified PUF tablets (Fig. 6). Thus, for maximum extraction of fluorescein from a solution with 1 tablet of polyurethane foam, 20 minutes is enough.

When fluorescein-modified PUF tablets were immersed in the solutions containing $5 \cdot 10^{-3}$ mol/L KBrO_3 , 0.01 mol/L H_2SO_4 , and bromide with concentrations from 5 to 80 mg/L, the formation of tetrabromofluorescein was observed, and the PUF tablets were colored pink. The maximum absorption of the product of the fluorescein bromination reaction on PUF corresponds to a wavelength of 541 nm (Fig. 2(3)). The holding time of fluorescein-modified PUF tablets in a solution containing KBrO_3 , H_2SO_4 , and Br^- (10 mg/L and 80 mg/L) was chosen based on measurements of the diffuse reflectance spectra of the tablets after the contact with the solution. The maximum color of the sorbent proportional to the bromide content in the solution was achieved after 20 minutes of sorption (Fig. 4b).

The estimation of the visual limit of quantification (LOQ) of Br^- was carried out according to the earlier described algorithm for I^- , and the results are presented in Table 2. A color scale was prepared corresponding to the Br^- content in a solution: 0, 5.0, and 10 mg/L and a control solution with the concentration of $c_{\text{set}} = 9.0$ mg/L. Out of 20 test results, the values of the standard deviation of the desired concentration (s_c) and the value of the LOQ were calculated—3.2 mg/L.

The coloration of PUF tablets after the test reaction of bromination of fluorescein immobilized on PUF remains stable for one week and is linearly related to the bromide ion concentration in the range of 5–80 mg/L, the equation of the calibration function: $\Delta F = (0.014 \pm 0.002) \cdot c$ ($R^2 = 0.996$).

The technique for test determination of iodide and bromide ions in samples of highly mineralized associated produced waters

For the test determination of iodide ions, a color scale is prepared (Fig. 7) in the range of iodide contents of 0.5–16 mg/L in such

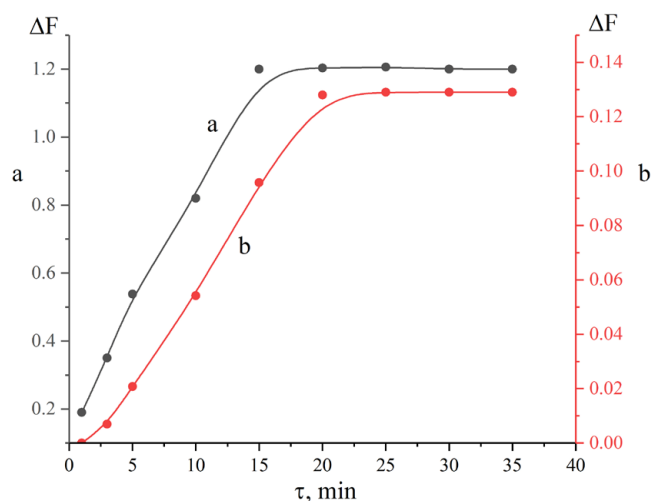


Fig. 4. Dependence of the Gurevich–Kubelka–Munk function on the sorption time: a, molecular iodine from the solution containing 0.01 mol/L KIO_3 , 0.01 mol/L H_2SO_4 , and 8 mg/L I^- , $\lambda_{\text{max}} = 380$ nm; b, tetrabromofluorescein from the solution containing $5 \cdot 10^{-3}$ mol/L KBrO_3 , 0.01 mol/L H_2SO_4 , and 10 mg/L Br^- , $\lambda_{\text{max}} = 541$ nm.

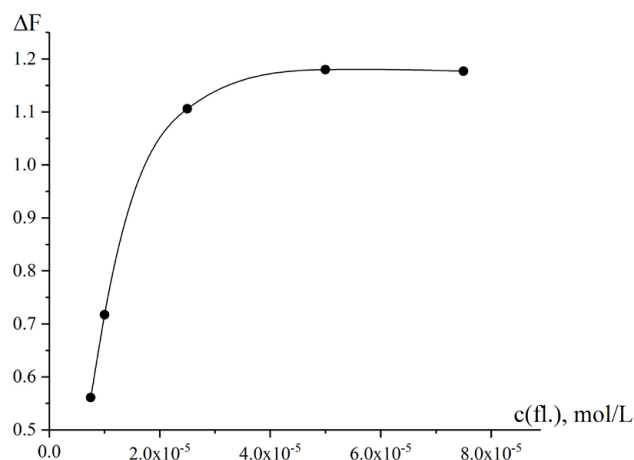


Fig. 5. Dependence of the Gurevich–Kubelka–Munk function on the concentration of fluorescein, $\lambda_{\text{max}} = 457$ nm.

Table 2. Results of the experimental evaluation of the value of quantification limit (LOQ) of Br^- visual determination using a color scale.

Added bromide, $c_{\text{set}} = 9.0$ mg/L	Bromide found, using a color scale, mg/L (n=20)		
	5.0	7.5	10
The number of observations	0	1	19
$s_c = 0.16$ mg/L; LOQ = $3s_c = 3.2$ mg/L			

Table 3. Results of determination of iodide and bromide content in formation waters (n=3, P=0.95).

Object	c(I ⁻), mg/L		c(Br ⁻), mg/L	
	Titration	Test method (dispersion range)	Titration	Test method (dispersion range)
APW №1	3.8 ± 0.3	3.75* (2.5–5)	61 ± 7	60** (41–82)
APW №2	16.0±0.08	13 (10.4–20.8)	130.3±0.5	126 (80–160)
APW №3	7.19±0.09	6 (5.2–10.4)	103.5±0.5	96 (80–160)

Notes: *Water is diluted 5 times; **water is diluted 5.5 times.

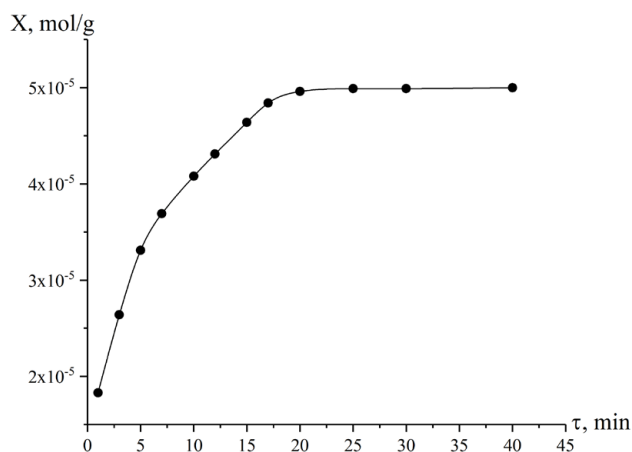


Fig. 6. Dependence of the sorbed amount of fluorescein substance per 1 g of polyurethane foam on the sorption time.

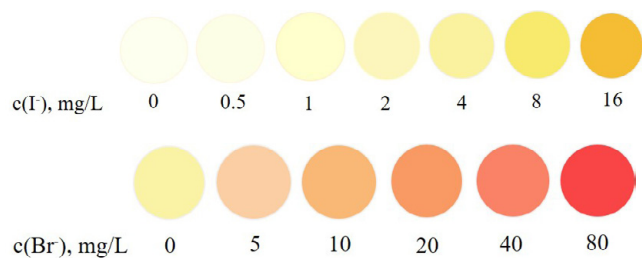


Fig. 7. Color scales for test determination: a, iodide; b, bromide ions in water.

a way that each subsequent concentration of iodide ions in the solution is twice as high as the previous one. To do this, the required aliquots of potassium iodide, 2.5 mL of 0.1 mol/L H₂SO₄, and 2.5 mL of 0.1 mol/L KIO₃ are added to 25-mL volumetric flasks and brought to the mark with distilled water. The prepared solutions are poured into weighing bottles, and 1 tablet of purified polyurethane foam is immersed in the solutions. Air bubbles are removed with a glass rod, and then, the solutions are placed on a mechanical vibration mixer for 20 minutes. After I₂ sorption, the polyurethane foam tablets are squeezed between sheets of filter paper and dried in the air.

For the analysis, 50 mL of filtered water sample is taken; 10 mL of 1 mol/L NaOH solution is added and mixed. The hydroxide precipitate is discarded. The filtrate is collected in a 100-mL measuring flask, acidified with sulfuric acid to pH 2, and brought to the mark with distilled water.

An aliquot of prepared water with a volume of 15 mL is placed into a 25-mL volumetric flask; 2.5 mL of 0.1 mol/L H₂SO₄ and 2.5 mL of 0.1 mol/L KIO₃ are added and brought to the mark with distilled water. Similar actions, just like in the case of preparing a color scale, are carried out. The concentration of iodide ions is determined using a color scale according to the recommendations (Reshetnyak et al., 2018).

To remove iodine, 2 tablets of purified polyurethane foam are added to the solution remaining after determining iodides and shaken for 20 minutes. The polyurethane foam tablets are removed and discarded, and the determination of bromide ions is carried out. An aliquot of 1–5 mL of the solution after removing iodine is placed in a 25-mL volumetric flask; 2.5 mL of 0.1 mol/L H₂SO₄ and 1.25 mL of 0.1 mol/L KBrO₃ are added and brought to the mark with distilled water. The solution is poured into a weighing bottle; 1 tablet of PUF with immobilized fluorescein is added and shaken for 20 minutes. The concentration of bromide ions is determined using a color scale.

It was established that the determination of iodides and bromides by the proposed method is not interfered by a 1000-fold excess of anions: SO₄²⁻, Cl⁻, F⁻, BO₂⁻, NO₃⁻, and S²⁻. A 100-fold excess of Br⁻ does not interfere with the determination of iodide ions.

The accuracy of the results of the separate determination of halides using the visual test method was verified by analyzing samples of APW using the proposed method and the oxidation–reduction titration method (Reznikov et al., 1970). The results of the determination are presented in Table 3. The results are correlated with each other, which confirms the correctness of the results of the determination according to the proposed method.

According to the proposed method, the determination of I⁻ and Br⁻ is cheaper and takes three times less time than using oxidation–reduction titration, since there is no need to prepare solutions of potassium hypochlorite, boric acid, sodium formate, ammonium molybdate, sodium thiosulfate, and its standardization. The stability of the color scales during the working week makes the analysis of a large number of samples of associated produced waters particularly rapid.

Conclusion

The results presented in the article show that the reactions of oxidation of iodide ions to molecular iodine with its subsequent extraction with PUF tablets and bromination of fluorescein immobilized on PUF can be successfully used for the rapid determination of iodide and bromide ions in their combined presence in formation waters associated with oil and gas production. The visual limit of quantification using the color scale was 3.2 mg/L for bromide ions and 0.48 mg/L for iodide ions. The accuracy of the proposed express control method was confirmed using the reference method of oxidation–reduction titration.

References

- Amourizi, F., Dashtian, K., Ghaedi, M. & Hajati S. (2020). Colorimetric determination of F⁻, Br⁻ and I⁻ ions by Ehrlich's bio-reagent oxidation over enzyme mimic like gold nanoparticles: Peroxidase-like activity and multivariate optimization. *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.*, 226(2), 117606. DOI: 10.1016/j.saa.2019.117606.
- Bothra, S., Kumar, R., Pati, R.K., Kuwar, A., Choi, H.-J. & Sahoo S.K. (2015). Virgin silver nanoparticles as colorimetric nanoprobe for simultaneous detection of iodide and bromide ion in aqueous medium. *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.*, 149(10), 122–126. DOI: 10.1016/j.saa.2015.04.059.
- Bowen, H.J.M. (1970). Absorption by Polyurethane Foams; New Method of Separation. *Journal of the Chemical Society A: Inorganic, Physical, Theoretical*, 72(7), 1082–1085. DOI: 10.1039/J19700001082.
- Buchberger, W. (1988). Determination of iodide and bromide by ion chromatography with post-column reaction detection. *J. Chromatogr. A*, 439(1), 129–135. DOI: 10.1016/S0021-9673(01)81681-2.
- Cheng, J., Jandik, P. & Avdalovic N. (2005). Pulsed amperometric detection of sulfide, cyanide, iodide, thiosulfate, bromide and thiocyanate with micro-fabricated disposable silver working electrodes in ion chromatography. *Anal. Chim. Acta*, 536(1–2), 267–274. DOI: 10.1016/j.aca.2004.12.039.
- De Souza, F.C., Vegas, C.G., Da Silva, D.A.I., Ribeiro, M.S., Cabral, M.F., De Melo, M.A., Mattos, R.M.T., Faria, R.B. & D'Elia E. (2016). Amperometric and potentiometric determination of iodide using carbon electrodes modified with salophen complex. *Journal of Electroanalytical Chemistry*, 783(12), 49–55. DOI: 10.1016/j.jelechem.2016.10.056.
- Dmitrienko, S.G., Sviridova, O.A., Pyatkova, L.N. & Senyavin V.M. (2002). Polyurethane foams as solid chromogenic reagents for diffuse reflectance spectroscopy. *Analytical and Bioanalytical Chemistry*, 374(10), 361–368. DOI: 10.1007/s00216-002-1513-6.
- Dobolyi, H.F. (1984). Field determination of bromide in water. *Anal. Chem.*, 56(12), 2961–2963. DOI: 10.1021/ac00278a076.
- Eickhorst, T. & Seubert A. (2004). Germanium dioxide as internal standard for simplified trace determination of bromate, bromide, iodate and iodide by on-line coupling ion chromatography-inductively coupled plasma mass spectrometry. *J. Chromatogr. A*, 1050(1), 103–109. DOI: 10.1016/j.chroma.2004.04.084.
- Fedan, D.A., Saranchina, N.V., Gavrilenko, N.A. & Proskurnin M.A. (2018). Solid-phase spectrophotometric iodometric determination of iodate in food salt using a polymethacrylate matrix (in Russian). *Analitika i Kontrol*, 22(1), 69–74. DOI: 10.15826/analitika.2018.22.1.009.
- Fu, L., Li, C., Li, Y., Chen, S., Long, Y. & Zeng R. (2017). Simultaneous determination of iodide and bromide using a novel LSPR fluorescent Ag nanocluster probe. *Sensors Actuators B: Chemical*, 240(3), 315–321. DOI: 10.1016/j.snb.2016.08.151.
- Fukushi, K. & Hiroyuki K. (1997). Simultaneous determination of bromide and iodide ions by capillary isotachopheresis using quaternary ammonium salts. *J. Chromatogr. A*, 760(2), 253–258. DOI: 10.1016/S0021-9673(96)00629-2.
- Fukushima, Y. & Aikawa S. (2021). Colorimetric detection of iodide ion by a nuclear fast red-based Hg²⁺ complex in aqueous media. *Tetrahedron Lett.*, 67(3), 152877. DOI: 10.1016/j.tetlet.2021.152877.
- García-Figueroa, A., Pena-Pereira, F., Lavilla, I., & Bendicho C. (2017). Headspace single-drop microextraction coupled with microvolume fluorospectrometry for highly sensitive determination of bromide. *Talanta*, 170(8), 9–14. DOI: 10.1016/j.talanta.2017.03.090.
- Geddes, C.D. (2000). Optical thin film polymeric sensors for the determination of aqueous chloride, bromide and iodide ions at high pH, based on the quenching of aquorescence of two acridinium dyes. *Dyes and Pigments*, 45(3), 243–251. DOI: 10.1016/S0143-7208(00)00025-5.
- Gorbunova, M.O., Baulina, A.A., Kulyaginova, M.S., Apyari, V.V., Furletov, A.A., Garshev, A.V. & Dmitrienko S.G. (2019). Determination of iodide based on dynamic gas extraction and colorimetric detection by paper modified with silver triangular nanoplates. *Microchem. J.*, 145, 729–736. DOI: 10.1016/j.microc.2018.11.046.
- Liu, M., Fu, X., Lu, M., Liu, J., Xie, H., Wei, P., Zhang, W., Xie, Y. & Qi Y. (2023). Colorimetric and visual determination of iodide ions via morphology transition of gold nanobipyramids. *Anal. Biochem.*, 666(4), 115077. DOI: 10.1016/j.ab.2023.115077.
- Loh, L.J., Bandara, G.C., Weber, G.L. & Remcho V.T. (2015). Detection of water contamination from hydraulic fracturing wastewater: a μ PAD for bromide analysis in natural waters. *Analyst*, 140(16), 5501–5507. DOI: 10.1039/c5an00807g.
- Mehra, H.C. & Frankenberger W.T. (1990). Simultaneous Determination of Cyanide, Chloride, Bromide, and iodide in Environmental Samples Using Ion Chromatography with Amperometric Detection. *Microchem. J.*, 41(1), 93–97. DOI: 10.1016/0026-265X(90)90100-J.
- Niemets, N.M., Melnyk, A.P., Brusentceva, T.V. & Niemets O.D. (2019). On the technology for producing iodine from oilfield produced water of oil-and-gas condensate fields and environmental safety (in Ukrainian). *Bulletin of the National Technical University "KhPI". Series: Innovation researches in students' scientific work*, 21(1346), 42–50. DOI: 10.20998/2220-4784.2019.15.08.
- Pilipenko, A.T., Terletska, A.V. & Zui O.V. (1989). Determination of iodide and bromide by chemiluminescence methods coupled with dynamic gas extraction. *Fresenius' J. Anal. Chem.*, 335, 45–48. DOI: 10.1007/BF00482390.
- Rastegarzadeh, S., Pourreza, N. & Saeedi I. (2009). An optical redox chemical sensor for determination of iodide. *Talanta*, 77(3), 1032–1036. DOI: 10.1016/j.talanta.2008.08.002.
- Reddy-Noone, K., Jain, A. & Verma K.K. (2007). Liquid-phase microextraction–gas chromatography–mass spectrometry for the determination of bromate, iodate, bromide and iodide in high-chloride matrix. *J. Chromatogr. A*, 1148(2), 145–151. DOI: 10.1016/j.chroma.2007.03.027.
- Reshetnyak, E.A., Nemets, N.N., Shugaj, E.A. & Chernyshova O.S. (2018). Extraction-photometric and visual-test determination of boron in underground local-water of oil and gas condensate field (in Russian). *Methods and Objects of Chemical Analysis*, 13(2), 85–89. DOI: 10.17721/moca.2018.85-89.
- Reznikov, A.A., Mulikovskaya, E.P. & Sokolov I.Yu. (1970). *Methods of analysis of natural waters* (in Russian). Moscow: Nedra.
- Sanemasa, I., Yoshida, M. & Abe A. (2008). Uptake of Iodine and Bromine by Ion-Exchange Resins in Aqueous Solution. *Analytical Sciences*, 24(7), 921–924. DOI: 10.2116/analsci.24.921.
- Trohimenko, A.Yu. & Zaporozhets O.A. (2014). Determination of total iodine in samples with an organic matrix by solid-phase spectrophotometry. *Journal of Analytical Chemistry*, 69(5), 408–412. DOI: 10.1134/S1061934814030150.
- Trokhymenko, A. & Zaporozhets O. (2012). Stepwise extraction of iodine forms coexisting in aqueous solutions by polyurethane foams (in Ukrainian). *Lviv University Bulletin, Chemical Series*, 53, 185–191.
- Zhang, A., Wang, S., Du, L. & Cui H. (2000). Simultaneous determination of micro bromide and iodide by kinetic spectrophotometric method. *Anal. Lett.*, 33(11), 2321–2331. DOI: 10.1080/00032710008543192.
- Zhu, C., Bright, F.V. & Hieftje G.M. (1990). Simultaneous determination of bromide and iodide ions with a multiple fiber-optic fluorescence sensor. *Appl. Spectrosc.*, 44(1), 59–63. DOI: 10.1366/0003702904085813.
- Zuy, O.V. & Maznyia Yu.I. (2014). Determination of Bromide Ions in Waters by RGB-Colorimetry Using (in Russian). *Methods and Objects of Chemical Analysis*, 9(3), 121–124. DOI: 10.17721/moca.2014.121-124.