# In-Vessel Headspace Liquid Phase Microextraction Coupled to Spectrophotometry for Iodate Determination

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*A new, highly sensitive and selective method for the spectrophotometric determination of iodate is developed based on the in-vessel mode of headspace liquid phase microextraction (IV-HS-LPME). The approach involves converting iodate to vapor iodine with excess of iodide and extracting it into a 50 μL of 1 % potassium iodide, which exposed to the headspace in a specially designed vessel. The extraction proceeds from 8 mL of aqueous solution containing 0.24 mmol $L^{-1}$ of iodide and 0.5 mol $L^{-1}$ of $Na_2SO_4$ after injection of 2 mL of 25% $H_2SO_4$. The complete equilibrium is established after the aqueous solution stirred at 1200 rpm for 20 minutes. After that, the triiodide complex formed in the acceptor phase is withdrawn with a microsyringe and transferred to a 50 μL quartz micro cell with a 10 mm path length, where the absorbance is measured at 288 or 350 nm. The calibration graph is linear ($r^2$ = 0.9998) in the range of 4 to 180 μg $L^{-1}$ (as $IO_3^-$) with a detection limit of 1.5 μg $L^{-1}$. The developed method has a high precision of 0.5 – 1.4%. It was successfully applied to the determination of iodate in table salt, sea, and mineral water samples.*

**Keywords:** in-vessel headspace liquid phase microextraction, iodate determination, spectrophotometry

# Парофазна мікроекстракція у реактор, сполучена зі спектрофотометрією, для визначення йодату

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*Розроблений новий, високочутливий та селективний метод для спектрофотометричного визначення йодату, який ґрунтується на методі парофазної мікроекстракції у реактор. Цей підхід передбачає перетворення йодату у пару йоду з надлишком йодиду та екстракцію його 50 мкл 1% калій йодиду. Акцепторна фаза закріплена у спеціально розробленому реакторі над розчином аналіту у герметично закритій віалі. Екстракцію проводять з 8 мл водного розчину, що містить 0.24 моль/л йодиду та 0.5 моль/л $Na_2SO_4$, після введення 2 мл 25% $H_2SO_4$. Повна рівновага встановлюється після перемішування водного розчину при 1200 об/хв протягом 20 хвилин. Після цього розчин трийодидного комплексу, що утворюється в акцепторній фазі, відбирається мікрошприцом і переноситься в кварцову мікрокювету об'ємом 50 мкл з довжиною шляху 10 мм, де вимірюється його світлопоглинання при 288 або 350 нм. Градуювальний графік є лінійним ($r^2$ = 0.9998) в діапазоні від 4 до 180 мкг/л (як $IO_3^-$) з межею виявлення 1.5 мкг /л. Розроблений метод має високу точність 0.5 – 1.4%. Він був успішно застосований для визначення йодату у зразках кухонної солі, морської та мінеральної води.*

**Ключові слова:** парофазна мікроекстракція у реактор, визначення йодату, спектрофотометрія

Liquid-liquid extraction is a well-known pretreatment technique for separation and preconcentration of organic and inorganic analytes. However, it has a lot of disadvantages, including limitations in preconcentration factor and the use of big volumes of organic solvents, which makes liquid-liquid extraction costly, time-consuming, and not friendly to human and environment [1]. These challenges can be avoided using liquid phase microextraction (LPME). It utilizes a small amount of organic solvent, inexpensive and simple equipment, and provides high enrichment factors [2, 3].

Single-drop microextraction (SDME) is one of the operating modes in LPME, which can be used for the determination of various species in a large number of matrices [4-6]. In this technique, a microdrop of an organic solvent, suspended at the tip of a microsyringe needle, is immersed into a sample solution (direct immersion single drop microextraction, DI-SDME) or placed in a headspace above the sample solution (headspace single drop microextraction, HS-SDME). Then the sample solution is stirred at a set temperature for a fixed extraction time. When the extraction is complete, the drop is retracted into the needle and transferred into the instrument for the analysis. Theis et al. developed the headspace (HS) mode of LPME in 2001 as a new variant of LPME that combines the benefits of both LPME and conventional head-space sampling [7, 8].

HS-SDME suffers from some disadvantages, including the limited extraction volume that cannot exceed 1-3 μL, drop dislodgement, and solvent volatility. The low interfacial contact area between sample and extraction solvent contributes to the decrease in the extraction efficiency [9]. The noted drawbacks of this method can be partly eliminated by developing special tools for retaining the microdrop of extraction solvent or using new types of extracting solvents, such as deep eutectic solvents or ionic liquids [10].

Given these features, combining spectrophotometry with HS-SDME is difficult. [11, 12]. The use of micro-volume UV-vis spectrophotometers was proposed [11]. 1-2 μL of the extract is sufficient to measure the absorbance but the optical path used is short ~1 mm, the number of solvents, which can be used, is limited, and the device is of high cost. It was proposed by Zaruba et al. [13, 14] to hold an extraction phase in the hole of the optical probe tip. The risk of losing a microdrop is diminished, several operations, such as extraction, transfer of the extractant to the cuvette, absorbance measurement, are combined into one. However, the droplet volume remains limited, and the device itself is expensive and inaccessible, the number of solvents that can be used is reduced due to the requirement for their good adhesion to the material of the optical probe.

Iodine deficiency impairs thyroid hormone development and has a variety of negative consequences during a person's life cycle, which is referred to as iodine deficiency disorders (IDD) [15]. Iodization of salt is the standard method for treating iodine deficiency conditions, and it is used in over 120 countries around the world. Because of salt iodization, several countries across the world have successfully eliminated or made significant strides in controlling iodine deficiency disorders [16]. The amount of iodate in salt and food samples varies with environmental factors, mode of transport, packaging conditions, and cooking methods, so determining iodate in these samples is critical.

Many methods have been proposed for the determination of iodate [17], including spectrophotometry [18], flow injection analysis with spectrophotometric detection [19-21], ion chromatography [22], reversed-phase high-performance liquid chromatography [23], and chemiluminescence [24]. However, we found only two articles in the literature devoted to the spectrophotometric determination of iodate combined with LPME methods [25, 26].

In this work, a new recently proposed headspace microextraction technique called in-vessel headspace liquid phase microextraction (IV-HS-LPME) [27] was applied to develop highly sensitive and selective spectrophotometric method for the determination of iodate based on in situ iodine generation. It was proposed to place the extraction phase not at the end of the microsyringe, but in a specially designed vessel in the headspace above the analyzed solution. Thus, the main limitation of the previously existing approach was removed, which consisted of the fact that it was impossible to use volumes larger than 3-5 μL. Since virtually any volume of extraction solvent can be placed in the vessel, this approach is fully compatible with common accessories used in the spectrophotometric analysis, including micro- and ultra-micro cuvettes with a volume of 50-100 or 5-10 μL, respectively. The developed method was successfully applied to the determination of the iodate content in table salt and natural waters.

## Experimental part

*Chemicals.* All chemicals used were analytical reagent grade or higher and were not further purified. Double-distilled water was used throughout the study. A 25% sulfuric acid solution was obtained by diluting 34.0 mL of concentrated 96% sulfuric acid (Sumy Chim Prom, Sumy, Ukraine) to a volume in a 200 mL volumetric flask. A stock iodide solution (10 g $L^{-1}$) was prepared from potassium iodide (Merck, Darmstadt, Germany) and stored in a dark brown glass containers to protect the solutions from light. 7.1 g of $Na_2SO_4$ was dissolved and made up to volume with distilled water in a 25 mL volumetric flask to prepare a 2 mol $L^{-1}$ sodium sulfate solution. The salting-out effect was tested with two following salts: NaCl and $Na_2SO_4$ (Life Chemicals, Kyiv, Ukraine).

*Apparatus.* The absorption spectra were measured using an SF-46 UV-visible spectrophotometer (LOMO, St. Petersburg, Russia) with glass cuvettes with an optical path length of 10 mm. Micro-volume quartz cuvettes (Starna Scientific Ltd., UK) with a path length of 10 mm (50 μL) were used to measure the absorbance. A magnetic stirrer (RIVA-03.2, UOSlab, Ukraine) with heating and electronic speed control was used to mix the solutions. Experiments were performed in a 15 mL pharmacy vials equipped with a rubber stopper. A 220 μL plastic vessel was fixed with a wire in a rubber stopper to hold the acceptor phase. A glass vessel was also used instead of a


**Fig. 1.** Schematic representation of the different steps for the iodate determination by IV-HS-LPME combined with UV-Vis spectrophotometry: (A) In-vessel headspace liquid phase microextraction, (B) transfer of the microvolume of extracting phase to microcuvette, (C, D) measuring the absorbance in a spectrophotometer.



plastic one. There was no significant difference in the results. 100 µL microsyringe (Hamilton, Bonaduz Ltd., Switzerland) was used to deliver the solutions. The experimental setup is shown in Fig. 1.

*Procedure for iodate determination.* To a 15 mL glass pharmacy vial 5.0 mL of the sample containing from 0.02 to 1.0 µg of iodate, 0.2 mL of 0.1 % potassium iodide and 3 mL of 1.7 M sodium sulfate solution are added. 50 µL of 1 % KI are placed into the vessel fixed in the headspace of the sample. The vial is sealed and 2 mL of 25 % sulfuric acid are added to the solution with syringe. The solution is stirred at 1200 rpm for 20 minutes. After finishing the extraction, the acceptor phase is transferred with a microsyringe to a 50 µL quartz micro cell with a 10 mm path length. The absorbance is measured at 350 nm.

## Results and discussion

The first stage of the preconcentration methods, based on the headspace microextraction, is to convert the analyte into volatile derivatives. When determining any form of iodine for this purpose, the reaction between iodate and iodide, which occurs in an acid solution, is often used. It should be emphasized that only weak reducing agents such as iodide can reduce iodate to iodine.

In addition, this reaction offers good signal enhancement through chemical amplification (Eq. (1)). Several parameters were optimized for the studied procedure, including the composition of extracting solvent, the concentrations of iodide and sulfuric acid, and parameters that have an influence on the extraction efficiency, such as volume of donor or acceptor phases, stirring rate, and extraction time. The salting-out effect was studied, since it was shown in previous studies that salts affect the evaporation of iodine [27].

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3H_2O + 3I_2 \quad (1)$$

**Choosing the nature and the composition of extracting phase.** Several extracting solvents have been proposed to extract iodine in previous HS-LPME methods [28]. It was shown in one of our previous studies [27], that, compared to the other extracting phases, aqueous solution of 1 % potassium iodide yielded a higher absorbance. The triiodide complex is formed when absorbed iodine reacts with excess iodide. It has a high molar absorptivity coefficient of 25 800 $mol^{-1}$ L $cm^{-1}$ at a wavelength of 350 nm (Fig. 2). The stability constant of this complex is small and equal to 720 [29]. Fig. 3 shows the dependence of the analytical signal on KI concentration in the acceptor phase. It can be seen that a 1 % KI concentration is sufficient to completely shift the equilibrium towards the formation of triiodide.

**Effect of iodide concentration in donor phase on the evaporation of iodine.** The concentration of iodide required for the quantitative conversion of iodate to iodine was studied in the range from 0.003 to 0.470 mmol $L^{-1}$ (Fig. 4A). The analytical signal remains practically constant starting from 0.06 mmol $L^{-1}$. For further experiments, an iodide concentration of 0.24 mmol $L^{-1}$ was chosen as optimal.

**Effect of sulfuric acid concentration**. Sulfuric acid was chosen to acidify the reaction mixture according to reaction (1). The effect of acid concentration on iodine formation was studied by varying the $H_2SO_4$ concentration in the range from 0.06 to 1.8 mol $L^{-1}$, when all other conditions were kept fixed. Fig. 4B shows that starting from $H_2SO_4$ concentration of 0.4 mol $L^{-1}$, the dependence flattens out and the absorbance reaches a maximum. The optimal concentration was assumed to be 0.6 mol $L^{-1}$ $H_2SO_4$.

**Effect of stirring rate and extraction time.** Previous works have shown that when a microsyringe was used as a microdrop holder, an extraction time of more than 7 minutes led to a decrease in absorbance [30]. The depressive effect observed with longer microextraction time was attributed to an increase in the microdrop size as a result of water absorption, which, in turn, caused the extracted analyte to dilute. This behavior is one of the negative consequences inherent to the classic SDME approach. However, the behavior of the studied reaction is more common. Fig. 5A shows that 25 minutes is sufficient to complete the extraction process, after which the absorption remains constant over time. It should be also noted that with a decrease in the volume of the acceptor phase from 100 to 50 μL, the time of equilibration is reduced to 20 minutes.

The sample solution must be agitated to enhance mass transfer in the aqueous phase and cause the convection in the headspace. To achieve the maximum analytical signal, the stirring speed should be about 1000 rpm. A further increase in the mixing speed, as seen in Fig. 5B, leads to a hold in the growth of absorbance. The fact that a constant maximum absorbance was achieved for all performed optimizations indicates that complete equilibrium is established in the system under study, and the total extraction rate depends only on the processes occurring in the acceptor phase.

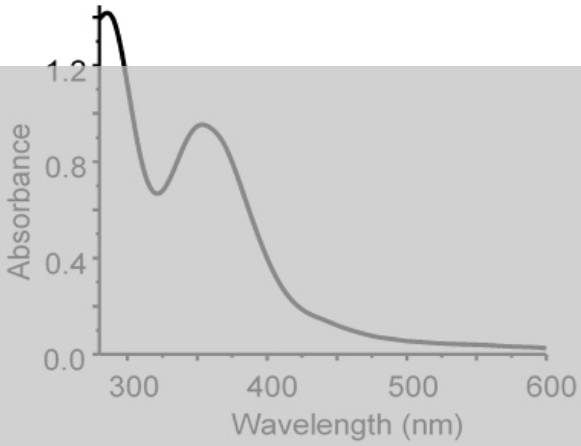



**Fig. 2.** Spectrum of triiodide complex formed in the acceptor phase. Donor phase – 5 mL containing 4.6 μM of iodate, $1.2\times10^{-4}$ M iodide, and 0.6 M $H_2SO_4$, acceptor phase – 100 μL of 0.1% KI, l = 1 cm.

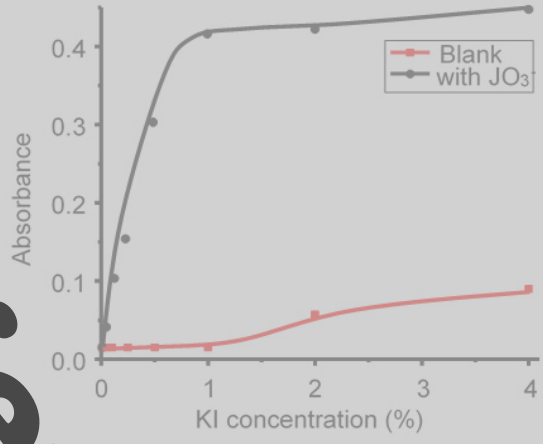
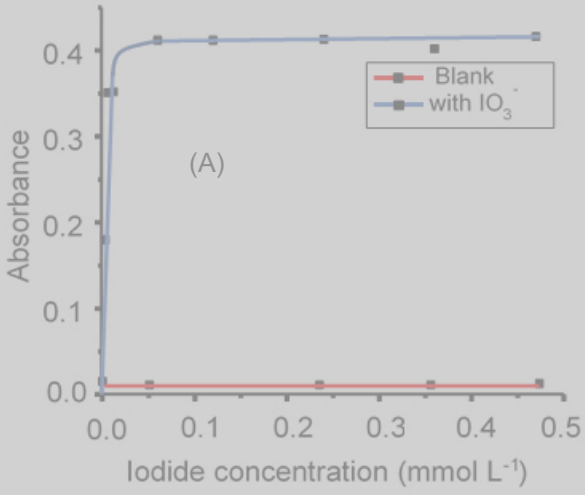



**Fig. 3.** Effect of the KI concentration in the acceptor phase on IV-HS-LPME of 2 μmol $L^{-1}$ of iodate.



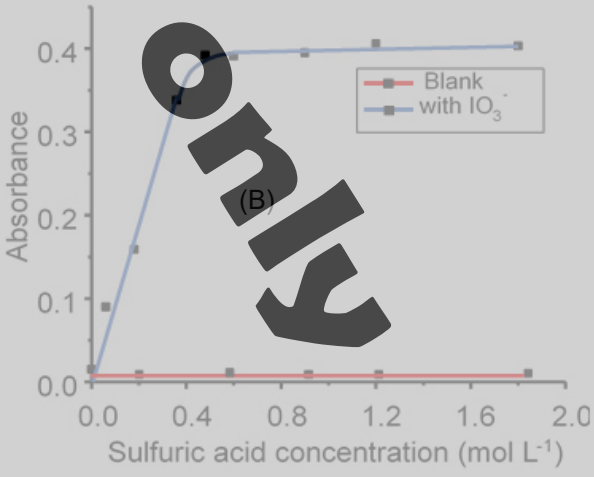




**Fig. 4.** Effect of iodide (A) and sulfuric acid (B) concentration in donor phase on absorbance of the acceptor phase.

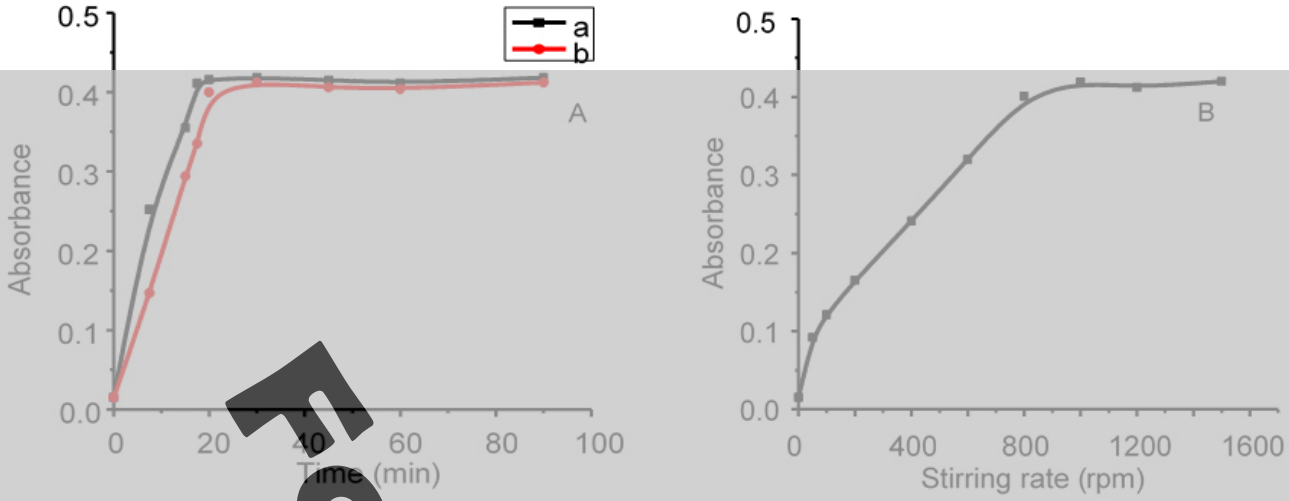



**Fig. 5.** Effect of time (A) and stirring speed (B) on the IV-HS-LPME of iodine for 10 (a) and 5 (b) mL of donor phase. Volume of acceptor phase: (A) 50 µL (a), 100 µL (b); (B) 100 µL. Concentration of iodate: (A) 0.5 µmol $L^{-1}$ (a), 2 µmol $L^{-1}$ (b); (B) 2 µmol $L^{-1}$



**Salting-out effect.** The effect of $Na_2SO_4$ and NaCl on iodine evaporation was studied. As shown in Fig. 6, the addition of 0.5 mol $L^{-1}$ of $Na_2SO_4$ to the analyte solution leads to a significant increase in the analytical signal by about 50 %. For the other salt tested (NaCl), absorbance decreases at concentrations above 0.7 mol $L^{-1}$.

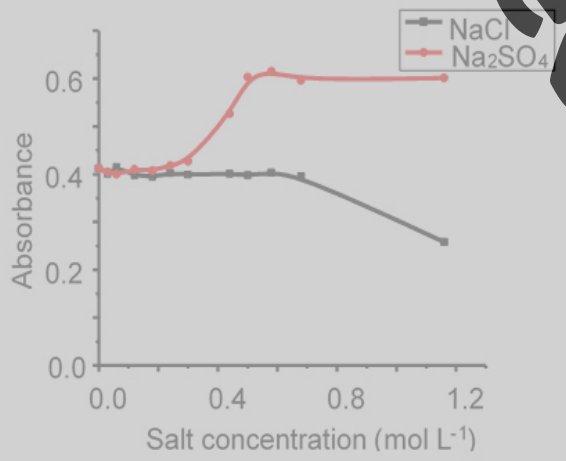



**Fig. 6.** Influence of salting-out effect on IV-HS-LPME of iodine.

**Influence of volumes of donor, headspace, and acceptor phases on extraction efficiency.** The volume of the extracting solvent has a significant impact on the preconcentration factor and extraction efficiency. The influence of the acceptor phase volume was studied in the range from 50 to 200 µL considering that minimum capacity of the microcuvettes used was 50 µL (Fig. 7). The maximum absorbance was obtained for the volume of the acceptor phase 50 µL, which was chosen as optimal.

In the studied three-phase system, the two equilibria are established between the donor phase and the headspace (Eq. (2)), as well as between the headspace and the acceptor phase (Eq. (3)). The corresponding distribution ratios were calculated by the nonlinear least-squares method. Sum of squares of the residuals between experimentally observed values of absorbance and its predicted values calculated using Eq. (4) was minimized.

$$D_1 = C_G^{eq} / C_D^{eq} \quad (2)$$

$$D_2 = C_A^{eq} / C_G^{eq} \quad (3)$$

The amount of analyte absorbed by the acceptor phase, $n = C_A^{eq} V_A$ can be expressed as [31]:

$$n = \frac{C_0 V_A V_D D_1 D_2}{D_1 D_2 V_A + D_2 V_G + V_D} \quad (4)$$

In these equations, $C_0$ is the initial concentration of the analyte in the donor solution; $C_D^{eq}$, $C_G^{eq}$ and $C_A^{eq}$ are the equilibrium concentrations of the analyte in the donor solution, the headspace, and the acceptor solution, respectively; $V_D$, $V_G$, and $V_A$ are the volumes of the donor phase, headspace, and acceptor phase, respectively.

For $D_1$ and $D_2$, the values of 1.0±0.1 and 15±2 were obtained, respectively. The distribution ratio of iodine, $D$, between the acceptor and donor phases can be calculated as the product of $D_1$ and $D_2$ [31], and it is equal to 15. The relatively low value of the distribution ratio $D$ for the extraction of iodine in the system under study shows that the extraction efficiency should greatly deteriorate with a decrease in the volume of the acceptor solution. This has indeed been observed experimentally. The extraction percentage was almost constant in the range from 50 to 100 µL and then increased, and what is important, in strict accordance with the values calculated by Eq. (4). The effect of the

volume of the donor phase on the absorbance of the acceptor phase was studied in the range from 2.5 to 10 mL using the vial with a total volume of 15 mL (Fig. 8). The extraction percentage was directly proportional to the volume of the donor phase and was in good agreement with the values calculated by the Eq. (4). 10 mL were chosen as the optimal total volume of the donor phase.

The enrichment factor usually depends on both the volumes of the donor and acceptor phases. However, in the system under study, the volume of the headspace also plays an important role. According to Eq. (4), a change in the headspace volume has a significant impact on the analytical signal. Due to the relatively high values of $D_2$ and volume of the headspace, the second term in the denominator of Eq. (4) becomes comparable with other terms, reflecting the increase in the contribution of the headspace volume. Fig. 8 shows that an increase in the volume of the donor phase causes an increase in the absorbance of the acceptor phase. At least part of this increase can be attributed to a decrease in the headspace volume. In the previous work [27], it was shown that an almost proportional decrease in absorbance is observed in the studied system with a decrease in the volume of headspace at constant volumes of the donor and acceptor phases. This emphasizes the importance of vial selection as well as the volume of the headspace in headspace microextraction.

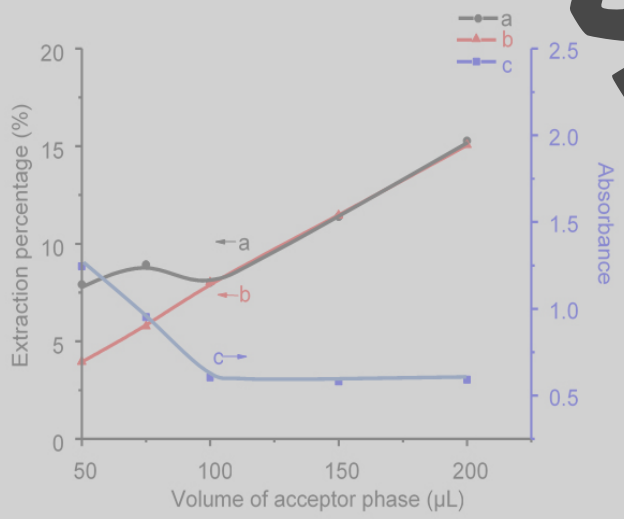



**Fig. 7.** Effect of acceptor phase volume on experimentally obtained (a) and calculated using Eq. (4) (b) extraction percentage of iodine or absorbance of acceptor phase (c) for extraction of 1 μM of iodate from 10 mL of donor phase.

**Calibration curve and detection limits for iodate determination.** Two calibration graphs were constructed using the measurements of absorbance at 288 and 350 nm. The following regression equations were calculated: A = (0.00700 ± 0.00006) × C for 350 nm ($r^2$ = 0.9999) and A = (0.01057 ± 0.00023) × C for 288 nm ($r^2$ = 0.9998) (where A is the absorbance and C is the concentration of $IO_3^-$ in μg $L^{-1}$). Under the optimized experimental conditions, both calibration graph for iodate determination were linear in the range from 4 to 180 μg $L^{-1}$ (as $IO_3^-$) (Fig. 9). The limit of detection of the method was 1.5 μg $L^{-1}$. The relative standard deviation values were in the range from 0.5 to 1.4 %. The preconcentration factor was calculated as the ratio between triiodide concentration in the acceptor phase and iodate concentration in the donor phase. In the conditions of the proposed method, it was 52.

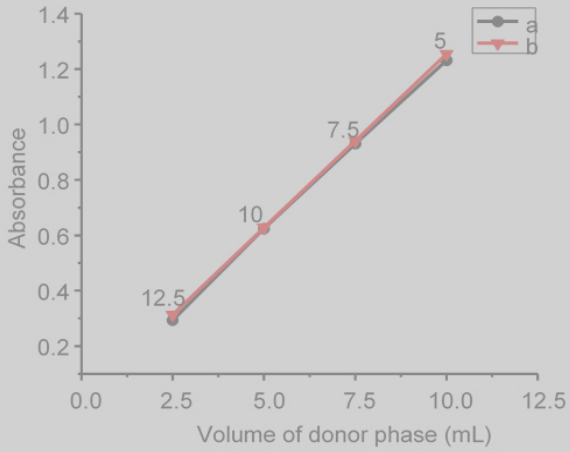



**Fig. 8.** Effect of donor phase volume on absorbance of acceptor phase for extraction of 2 μg iodate into 100 μL of acceptor phase in a vial with total volume of 15 mL. Numbers above points indicate volume of the headspace. Curve b represents the simulated absorbance values calculated using Eq. (4).

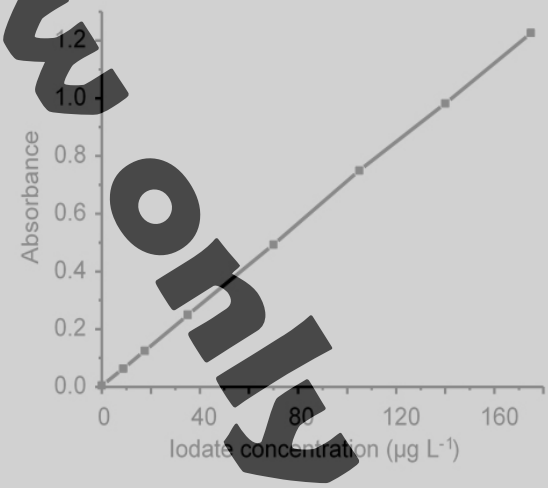



**Fig. 9.** Calibration curve for the spectrophotometric determination of iodate combined with IV-HS-LPME. Volumes of donor phase – 10 mL, headspace – 5 mL, acceptor phase – 50 μL of 1% KI. Composition of donor phase: C($H_2SO_4$) = 0.6 mol $L^{-1}$, C(KI) = 0.24 mmol $L^{-1}$, C($Na_2SO_4$) = 0.5 mol $L^{-1}$, stirring rate 1200 rpm, extraction time = 20 minutes, λ = 350 nm, l = 1 cm.

The developed method has higher analytical characteristics in comparison with the existing methods for the determination of iodate with spectrophotometric detection (Table 1). It has a much higher sensitivity than spectrophotometric methods based on the formation of a complex of iodine with starch [32] or the interaction of iodine with variamine blue [33]. Flow injection methods based on a similar chemistry have one to two orders of magnitude lower detection limits than the proposed one [19-21].

Two existing spectrophotometric methods for the determination of iodate with preliminary liquid-phase microextraction have approximately the same sensitivity as that proposed by us. However, it should be borne in mind that the VALLME method, based on direct contact between the aqueous and organic phases, has an extraction efficiency close to 100 % [25]. It suffers from the influence of a dirty or complex matrix and the presence of solid particles in the sample. The extraction time is short, but the total time for all operations such as centrifugation is more than 12 minutes. In addition, the method developed by us belongs to the methods of "Green Chemistry" and does not use organic solvents.

The second existing method is based on headspace mode of SDME and therefore takes full advantages of the complete separation of the sample from the matrix. However, as mentioned above, it suffers from limitations in extractant volume, drop dislodgement, and solvent volatility. Despite the large difference in the volumes of the used acceptor phase (50 µL against 2.5 µL in [26]) the obtained sensitivity was at the same level. This can be explained by the higher extraction efficiency achieved in the developed technique. In the proposed method, you can use any stirring rate and wait as long as necessary without fear that the microdrop may fall. Therefore, a state of equilibrium and the highest possible analytical signal are always achieved. In addition, the small optical path used in the micro-volume spectrophotometer contributes to a decrease in sensitivity.

**Study of interference in the iodate determination.** The interfering effect of some typical ions present in natural waters on iodate determination was studied. The concentration of iodate in aqueous sample was kept constant at $10^{-6}$ mol $L^{-1}$, while the amount of interfering ion was varied. It was found that when $K^+$, $Na^+$, $Mg^{2+}$, $Ca^{2+}$, $HCO_3^-$, $SO_4^{2-}$, $Cl^-$ are present at least 1000-fold excess they did not interfere with the determination of iodate. The obtained results indicate that 0.06 g $L^{-1}$ concentration of iodide did not cause any influence on the analytical signal. NaCl concentrations of 0.8 and 1.2 mol $L^{-1}$ had a strong depressing effect on iodate determination (20 and 60 %, respectively). The most serious interference in the determination of iodate cause bromates. To reduce bromate interference, pre-reduction was required while iodate remained unchanged. Bromate was reduced by Fe(II) in 20 minutes at room temperature [26]. Bromide concentrations may be as high as 100 mg $L^{-1}$, that is higher than typically found in natural waters. Nitrite concentrations up to 0.05 mg $L^{-1}$ were allowed. 50 mg $L^{-1}$ of Fe(III) did not cause any influence on the analytical signal.

**Determination of iodate in iodized salt and water samples.** The proposed method was applied to the determination of the iodate content in table salt and natural waters. Analytical results are shown in Table 2. Iodate levels in the three water samples analyzed (tap water, bottled water, and seawater) were found to be below the quantification limit. To assess the effect of the matrix, a recovery study was conducted. Table 2 shows that recoveries ranged from 99.9 to 101.6 %. Iodate was determined in table iodized salt without pre-treatment. A 50 mg sample of table salt was dissolved in 5 mL of distilled water and directly analyzed. The results obtained are in the range indicated by the manufacturer and are in good agreement with the results obtained by an independent method based on direct spectrophotometric determination after the release of iodine and interaction with variamine blue.



**Table 2.** Determination of iodate ($IO_3^-$) content in real samples (P = 0.95, n = 5).

| Sample | Iodate added (µg $L^{-1}$) | Iodate found (µg $L^{-1}$) | $S_r$ | Recovery (%) |
|---|---|---|---|---|
| Tap water | - | <LOQ* | | |
| | 87.5 | 87.4 ± 0.2 | 0.027 | 99.9 |
| Bottled water | - | <LOQ* | | |
| | 87.5 | 87.6 ± 0.3 | 0.032 | 100.1 |
| Seawater (Sea of Azov) | - | <LOQ* | | |
| | 87.5 | 87.8 ± 0.4 | 0.038 | 101.3 |
| Iodized salt (Artyomsalt)** | - | 49.8 ± 2.1 mg $kg^{-1}$ | 0.052 | |
| | - | 50.4 ± 1.4 mg $kg^{-1}$ *** | 0.035 | |
| | 43.5 mg $kg^{-1}$ | 90.9 ± 4.8 mg $kg^{-1}$ | 0.074 | 105.8 |

* LOQ = 4 µg $L^{-1}$

** Content specified by the manufacturer 40 ± 15 mg $kg^{-1}$ (as $I^-$)

*** Determined by method described in [33]

**Table 1.** Comparison of the proposed method with reported UV-Vis spectrophotometric techniques for the determination of iodate.

| Technique | Method | LOD (μg $L^{-1}$) | Linear range (μg $L^{-1}$) | RSD (%) | Extraction time, min | Volume of sample solution (mL) | Volume of extracting solvent | Ref |
|---|---|---|---|---|---|---|---|---|
| FI-UV–vis | The oxidation of iodide by the iodate to iodine. Formation of triiodide in the presence of starch. | 330 | 875–7000 | 0.66 | 1 | 5 | - | [19] |
| FI-UV–vis | Reaction of iodate with iodide at pH 3.5. | 50 | 50–10000 | 0.65–0.8 | 3 | 300 μL | - | [20] |
| Reverse FI-UV–vis | The iodate reacts with excess iodide in acidic medium to form tri-iodide. | 8 | 20–3000 | 0.9 | 0.6 | 25 | - | [21] |
| VALLME | The extraction of iodine as a result of iodate reduction with TBA-I in acid solution and formation of triiodide. | 1.5 | 5.2–88 | 1.9-8.6 | 0.33 | 4.2 | 150 μL of amyl acetate | [25] |
| μVolume HS-SDME | The conversion of iodate into vapor iodine and its extraction with a single drop of N,N dimethylformamide (DMFA). | 1.5 | 7.5–175 | 4.2 | 7 | 10 | 2.5 μL of DMFA | [26] |
| UV–vis | Oxidation the iodine species to iodate with permanganate, acidification, reaction with starch-iodide reagent and measuring the absorbance of the starch-iodine complex. | 10 | 10-200 | - | 15 | 10 | - | [32] |
| UV–vis | Reaction between iodate and excess iodide in acid solution. Reaction of iodine with variamine blue (VB) dye. | 200 | 200-3000 | | 5 | 5.75 | - | [33] |
| IV-HS-LPME | Reaction between iodate and excess iodide in 0.4 M $H_2SO_4$ and extraction of the volatile iodine into 50 μL of 1% KI | 1.5 | 4-180 | 0.5–1.4 | 20 | 4.8 | 50 μL of 1% KI | This work |

## Conclusions

In this work, a new, highly sensitive and selective spectrophotometric method for the determination of iodate with previous preconcentration was developed, based on a new microextraction technique termed in-vessel headspace liquid phase microextraction ((IV-HS-LPME)). The proposed procedure is based on the conversion of iodate into volatile iodine with an excess of iodide, its transfer first into the headspace and, finally, the absorption by 1% KI solution with the formation of triiodide ion. The absorbance of triiodide is measured in a microcuvette with a volume of 50 µL.

The most of disadvantages inherent to the previous approach, including too low volume of extracting phase or danger of microdrop dislodgement, are completely eliminated in the proposed method. Thus, the IV-HS-LPME method is fully compatible with common instruments and accessories used in a spectrophotometry. It has higher extraction efficiency comparing with the approach using the suspended microdrop.

Compared to a few LPME methods with spectrophotometric detection for the determination of iodate, the proposed technique has the same sensitivity and potential for further improvement, taking into account the possibilities of increasing the volume ratio of the donor and acceptor phases. In any case, the main advantages of headspace methods include complete separation from the sample matrix and high selectivity. It was shown that the matrix components of analytical samples such as mineral water, seawater, and table salt had no effect on the accuracy of iodate determination using the proposed method.



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