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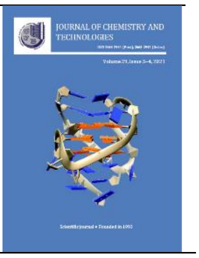

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COMBINATION OF PRECONCENTRATION BY IN-VESSEL HEADSPACE LIQUID-PHASE MICROEXTRACTION AND SPECTROPHOTOMETRY FOR DETERMINATION OF NITRITE IN NATURAL WATERS

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Abstract

A new, simple, highly sensitive and selective method for the spectrophotometric determination of nitrite based on the method of in-vessel headspace liquid-phase microextraction has been developed. It includes the release of iodine vapor in the reaction of nitrite with an excess of iodide and its absorption by 50 µL of 1% potassium iodide. The acceptor phase is located in the headspace above the solution in a specially designed container. Extraction of iodine takes place from 10 mL of an aqueous solution containing 2 mL of 25% H_2SO_4, after the introduction of 0.25 mL of 1% KI. Full equilibrium is established after stirring the aqueous solution at 1200 rpm for 17 minutes. After that, the triiodide complex formed in the acceptor phase is removed with a microsyringe and transferred into a quartz microcuvette with a volume of 50 µL and an optical path of 10 mm, in which the absorbance of the solution of the acceptor phase is measured at 350 nm. The calibration graph is linear ($r^2 = 0.9997$) in the range from 3 to 120 µg L^{-1} (as NO_2^-) with a detection limit of 1.0 µg L^{-1}. The developed method was successfully applied to determine the content of nitrite ions in mine waters and is characterized by a higher sensitivity and lower influence of large amounts of metal ions in comparison with the standard method based on the use of the Griess reagent.

Keywords: In-vessel headspace liquid phase microextraction; nitrite determination; spectrophotometry; mine waters

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КОМБІНАЦІЯ КОНЦЕНТРУВАННЯ МЕТОДОМ ПАРОФАЗНОЇ МІКРОЕКСТРАКЦІЇ У РЕАКТОР ТА СПЕКТРОФОТОМЕТРІЇ ДЛЯ ВИЗНАЧЕННЯ НІТРИТУ У ПРИРОДНИХ ВОДАХ

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Анотація

Розроблено новий, простий, високочутливий і селективний метод для спектрофотометричного визначення нітриту, який ґрунтується на методі парофазної рідинної мікроекстракції у реактор. Він включає виділення парів йоду в реакції нітриту з надлишком йодиду і поглинання 50 мкл 1% йодиду калію, причому акцепторна фаза розміщується в газовій фазі над розчином в спеціально сконструйованій ємності. Екстракційне витягнення йоду проходить з 10 мл водного розчину, що містить 2 мл 25% H_2SO_4, після введення 0.25 мл 1% KI. Повна рівновага встановлюється після перемішування водного розчину при 1200 об / хв протягом 17 хвилин. Після цього трийодидний комплекс, що утворився в акцепторній фазі, відбирається мікрошприцем і переноситься в кварцову мікрокювету об'ємом 50 мкл з товщиною поглинаючого шару 10 мм, в якій вимірюється оптична густина розчину акцепторної фази при 350 нм. Градуювальний графік є лінійним ($r^2 = 0.9997$) в діапазоні від 3 до 120 мкг $л^{-1}$ (як NO_2^-) з межею виявлення 1.0 мкг $л^{-1}$. Розроблений метод був успішно застосований для визначення вмісту нітрит-іонів в шахтних водах і характеризується більш високою чутливістю і меншим впливом великої кількості іонів металів в порівнянні зі стандартним методом, який ґрунтується на використанні реактиву Грісса.

Ключові слова: парофазна мікроекстракція у реактор, визначення нітриту, спектрофотометрія, шахтні води.

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КОМБИНАЦИЯ КОНЦЕНТРИРОВАНИЯ МЕТОДОМ ПАРОФАЗНОЙ МИКРОЭКСТРАКЦИИ В РЕАКТОР И СПЕКТРОФОТОМЕТРИИ ДЛЯ ОПРЕДЕЛЕНИЯ НИТРИТА В ПРИРОДНЫХ ВОДАХ

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Аннотация

Разработан новый, простой, высокочувствительный и селективный метод для спектрофотометрического определения нитрита, основанный на методе парофазной жидкостной микроэкстракции в реактор. Он включает выделение паров йода в реакции нитрита с избытком йодида и поглощение 50 мкл 1% йодида калия, причем фаза акцептора размещается в газовой фазе над раствором в специально сконструированной емкости. Экстракционное извлечение йода проходит из 10 мл водного раствора, содержащего 2 мл 25% H_2SO_4, после введения 0.25 мл 1% KI. Полное равновесие устанавливается после перемешивания водного раствора при 1200 об / мин в течение 17 минут. После этого трийодидный комплекс, образовавшийся в акцепторной фазе, извлекается микрошприцом и переносится в кварцевую микрокювету объемом 50 мкл с толщиной поглощающего слоя 10 мм, в которой измеряется оптическая плотность раствора акцепторной фазы при 350 нм. Градуировочный график является линейным (r^2 = 0.9997) в диапазоне от 3 до 120 мкг $л^{-1}$ (как NO_2^-) с пределом обнаружения 1.0 мкг $л^{-1}$. Разработанный метод был успешно применен для определения содержания нитрит-ионов в шахтных водах и характеризуется более высокой чувствительностью и меньшим влиянием больших количеств ионов металлов по сравнению со стандартным методом, основанным на использовании реактива Грисса.

Ключевые слова: парофазная микроэкстракция в реактор; определение нитрита; спектрофотометрия; шахтные воды.

Introduction

The hyphenated or hybrid techniques are developed from the coupling of two or three techniques in order to improve the capabilities of analytical methods and broaden their applications. Recently we have proposed new method for the separation and preconcentration of volatile and semi-volatile compounds – in-vessel headspace liquid-liquid microextraction, which can be combined practically with any detection technique [1; 2]. In this approach, it was proposed to held the acceptor phase in a specially designed vessel suspended above the analyzed solution in a hermetically closed vial. However, generally accepted method of headspace liquid-phase microextraction (HS-LPME) uses configuration in which the acceptor phase is suspended from the tip of a microsyringe needle [3–6]. In this way, only up to 5 µL of extracting solvent can be retained. This volume meets the requirements of such important methods for the determination of volatile species as gas chromatography or capillary electrophoresis, but combination with most other analytical techniques is impossible or very limited. These limitations have been partially circumvented using various approaches. It was suggested to keep the acceptor phase inside of a syringe [7] or a glass tube [8]. The retained volume was increased by equipping the syringe needle with a small funnel [9], by using an ionic liquid [10] and other methods. With the help of an optical probe, a higher stability of the solvent drop was achieved, which made it possible to conduct online monitoring of the analytical signal [11; 12]. Nevertheless, the volume of the extractant is limited to 20–30 µL, and the optical probe itself cannot be attributed to a cheap device.

The placement of the acceptor phase in a vessel allows to flexibly change its volume. Existing accessories for spectrophotometry are represented, in particular, by micro cuvettes with a volume of 50 or 100 µL or ultramicro cuvettes with a volume of 5 or 10 µL. Previous studies [1; 2] have shown that the extraction efficiency remains at the same level as in previously developed analytical methods. Moreover, a state of equilibrium can be achieved in all cases, which allows achieving the highest possible sensitivity and good reproducibility of the assay. The method was used to determine the forms of iodine, including iodide and iodate. It is of interest to evaluate the capabilities of the IV-HS-LPME method for the determination of other species.

Among the various anionic analytes, the nitrite ion is one of the most important because of its biological and environmental effects. Nitrite is widely used as a preservative in food, fertilizers, detergents, wood pulp and dyes, and thus can be released into the environment, contaminating soil, groundwater, rivers and lakes. The important role of nitrite in the production of N-nitrosamines, some of which have been shown to be carcinogens in humans, is well known. In addition, nitrite ions can markedly reduce the blood's ability to carry oxygen through the irreversible conversion of oxyhemoglobin to methemoglobin and leads to methemoglobinemia in infants. According to the World Health Organization, the maximum allowable amount of nitrite ion in drinking water is 0.1 mg L^{-1} [13]. High levels of nitrite ion can lead to a wide range of adverse health effects and ecosystem degradation. For example, nitrite can damage the nervous system, spleen, liver and kidneys of fish at concentrations as low as 0.25 µg g^{-1}. Therefore, it is very important to develop a fast, selective and simple method for the determination of nitrite in trace amounts.

Several reports have been published on the determination of nitrite, including chromatography [14], electroanalytical methods [15], and capillary electrophoresis [16]. Some of these methods have low selectivity. Other methods require expensive and complex instruments or reagents, while others require complex and time-consuming separation procedures. However, spectroscopic methods are the most widely used for the nitrite determination, especially because of their simplicity and availability [17]. Among them, spectrophotometric methods based on the Griess assay are widely used for water analysis [18, 19]. Nevertheless, Griess standard nitrite colorimetric assay is often not sensitive enough to be applied directly to water samples. Therefore, to circumvent the low sensitivity of spectrophotometric methods, several sample preparation techniques have been developed, such as solid-phase extraction (SPE) [19; 20] or cloud point extraction (CPE) [21; 22] for separation and preconcentration of nitrite in aqueous matrices before spectrophotometric detection. However, these methods of sample preparation are associated with a relatively high consumption of reagents and, as a consequence, high waste generation. Flow injection [20] and sequential injection systems (SIA) [23] were used to increase sample throughput. Liquid-liquid microextraction methods have already been actively used for the preconcentration and separation of nitrite, which will be discussed later in this article.

The aim of the study was to develop a simple, relatively fast, selective and sensitive spectrophotometric method for the determination of nitrite in natural waters using the recently developed new IV-HS-LPME approach for preconcentration and separation.

Experimental part

Reagents and equipment. 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 container to protect the solutions from light. 172.5 mg of $NaNO_2$ was dissolved and made up to volume with distilled water in a 25 mL volumetric flask to prepare a 0.1 mol L^{-1} sodium nitrite solution. 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).

Absorbance and absorption spectra were measured on an SF-46 spectrophotometer (LOMO, St. Petersburg, Russia) equipped 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 (Fig. 1). A plastic or glass vessel designed to hold the acceptor phase was secured with a wire in a rubber stopper. The pH was monitored on a pH-150 MI pH meter with an ES-10601 glass indicator electrode and an ESD-10101 silver chloride reference electrode.

Procedure for nitrite determination. 10 mL of the sample containing from 3 to 120 µg L^{-1} of nitrite are transferred to a 15 mL glass pharmacy vial. 50 µL of 1 % KI are placed into the vessel fixed in the headspace of the sample. Then the sample solution is acidified with 2 mL of 25% sulfuric acid. To initiate the formation of volatile iodine, 0.25 mL of 1% potassium iodide solution is injected with syringe into the sample solution. Then, the solution is stirred at 1200 rpm for 17 minutes. After finishing the extraction, the acceptor phase is transferred with a micro syringe to a 50 µL quartz micro cell with a 10 mm path length. The absorbance is measured at 350 nm.

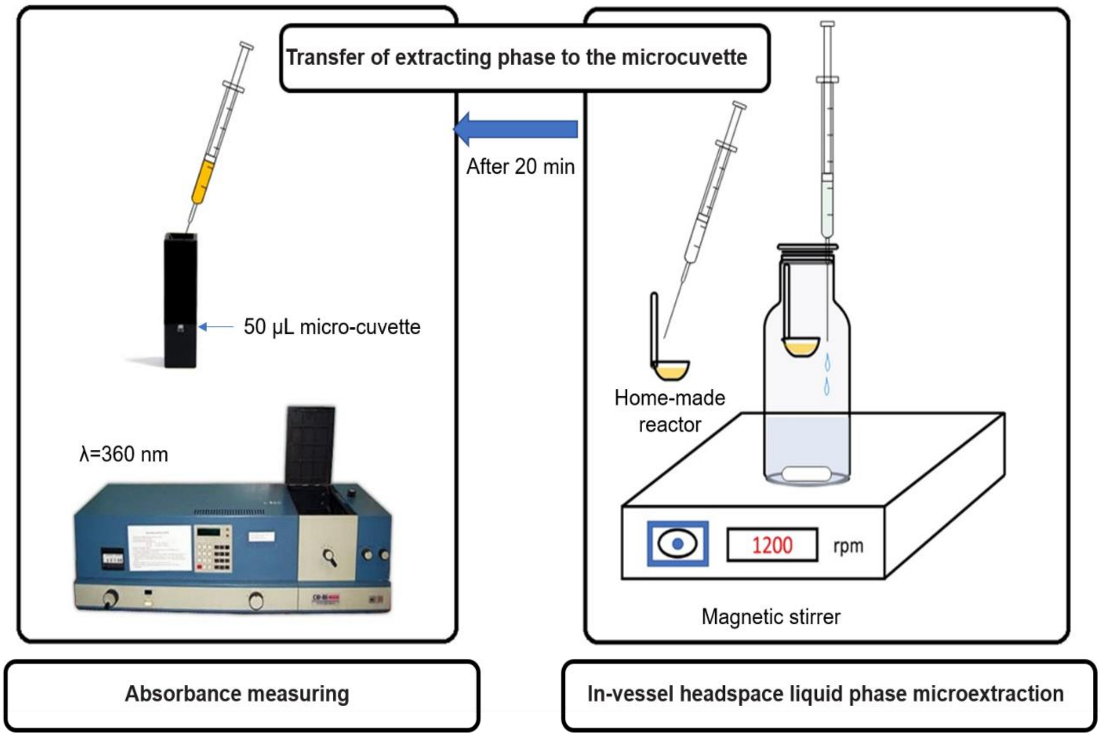

Fig. 1. Setup for the spectrophotometric determination of nitrite ions with preconcentration by IV-HS-LPME method

Results and its discussion

Chemistry of the method and choice of extractant. In this work, we proposed to determine nitrite by a method that involves the conversion of iodide into volatile iodine in reaction with nitrite and its subsequent absorption by a solution of iodide with the formation of a triiodide complex. In previous experiments, we have chosen the most suitable extractant. We tried to use a solution of starch, toluene, dimethylformamide (DMF), and iodide as an acceptor phase. The use of DMF was previously recommended [24]. In this solvent, iodine is converted to triiodide, which has the most intense spectrum of all forms of iodine. We confirmed this conclusion, but, unfortunately, the solvent we used was rather contaminated and had a strong background absorbance. So, we gave it up and found a new system that was even more efficient. When iodide reacts with iodine, the highly absorbing triiodide is formed.

The determination is based on the reaction of nitrite with an excess iodide.

$$2NO_2^- + 6I^- + 8H^+ = N_2 + 3I_2\uparrow + 4H_2O \qquad (1)$$

During this reaction, iodine is generated in an amount equivalent to the amount of nitrite present in the sample to be analyzed. Iodine is a volatile substance. Consequently, under the conditions of the analysis, most of it enters the gas phase above the solution, and then dissolves in the solution of the acceptor phase. The acceptor phase contains iodide, which forms a stable compound with iodine, triiodide, according to the reaction

$$I_2 + I^- = I_3^- \qquad (2)$$

Triiodide is an intense yellow-brown substance. The spectrum of this substance has two intense absorption bands at 288 and 360 nm [2]. Although at 288 nm the molar absorption coefficient is higher – 38790 mol^{-1} L cm^{-1}, it is still more convenient to use a wavelength of 350 nm (ε = 25750 mol^{-1} L cm^{-1}), because at this wavelength glass can be used, and not quartz cuvettes, as well as simpler devices that do not have a deuterium lamp (a source of ultraviolet radiation). In addition, as we showed in [2], the resulting sensitivity was similar for both wavelengths.

In previous experiments, we used another direct reaction for the determination of nitrite with the formation of a mixture of volatile nitrogen oxides in the reaction with acid.

$$NaNO_2 + HCl = NaCl + HNO_2 \qquad (3)$$

$$2HNO_2 = N_2O_3 + H_2O = NO\uparrow + NO_2\uparrow + H_2O \qquad (4)$$

But in this reaction it was not so easy to find an acceptor solution that would give an intense color with a mixture of nitrogen oxides. The concentration of iodide in the acceptor phase was taken to be 1 %, since in previous works [1, 2] it was found that at this concentration the equilibrium in reaction (2) completely shifts towards the formation of the triiodide complex.

Influence of the concentration of iodide in the donor phase on the evaporation of iodine. The concentration of iodide required for the quantitative conversion of iodide to iodine was studied in the range from 0.03 to 6 mmol L^{-1} (Fig. 2A). The analytical signal remained practically constant, starting at 1.0 mmol L^{-1}. For further experiments, the iodide concentration of 1.5 mmol L^{-1} was chosen as optimal.

Influence of the concentration of sulfuric acid. 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 concentration of H_2SO_4 in the range from 0.075 to 0.9 mol L^{-1}, when all other conditions were kept fixed. Fig. 2B shows that starting with an H_2SO_4 concentration of 0.5 mol L^{-1}, the dependence flattens out and the absorption reaches a maximum. The optimal concentration was taken as 0.6 mol L^{-1} H_2SO_4.

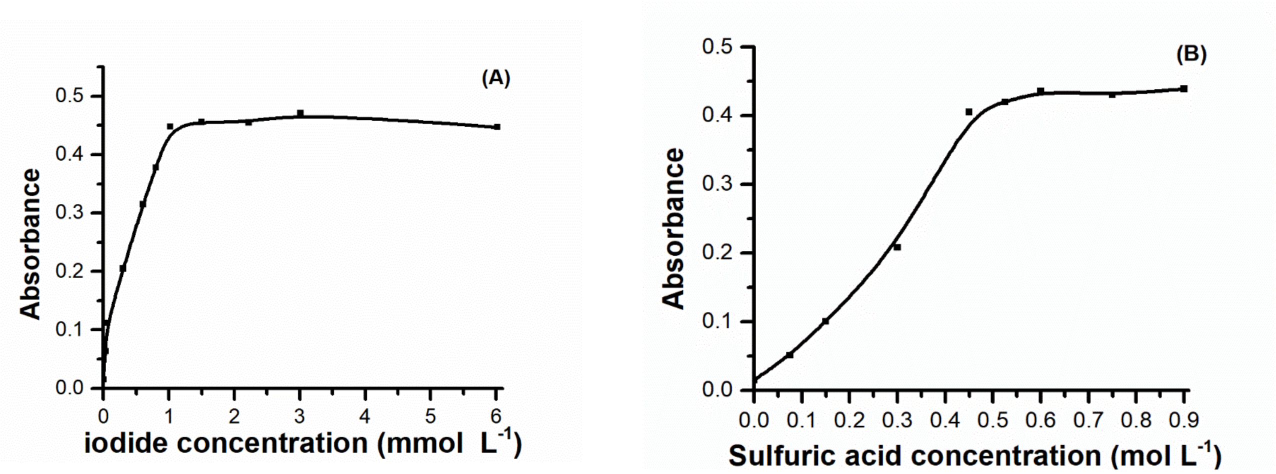

Fig. 2. Influence of iodide (A) and sulfuric acid (B) concentration on absorbance of acceptor phase in the determination of nitrite with IV-HS-LPME preconcentration. Volume of acceptor phase: (A) 100 µL; (B) 100 µL. Concentration of nitrite: (A) 92 µg L^{-1}; (B) 92 µg L^{-1}

Effect of stirring time. The extraction time is one of decisive factors that affect the total time of the entire analytical procedure. In the IV-HS-LPME method, it is always possible to achieve a state of equilibrium. As confirmed in this study, in all cases we observed a plateau on the optimization curves. This proves that overall extraction rate is determined only by only one of the stages. This stage is the absorption of volatile products (iodine vapor) by the solution of the acceptor phase. We investigated the dependence of the extraction time for two volumes of the acceptor phase, 50 and 100 µL. As can be seen from Fig. 3A, the extraction time decreases with decreasing volume of the acceptor phase. It was equal to 15 and 20 min, respectively. It is clear that the smaller the volume of the acceptor phase, the faster the diffusion process proceeds.

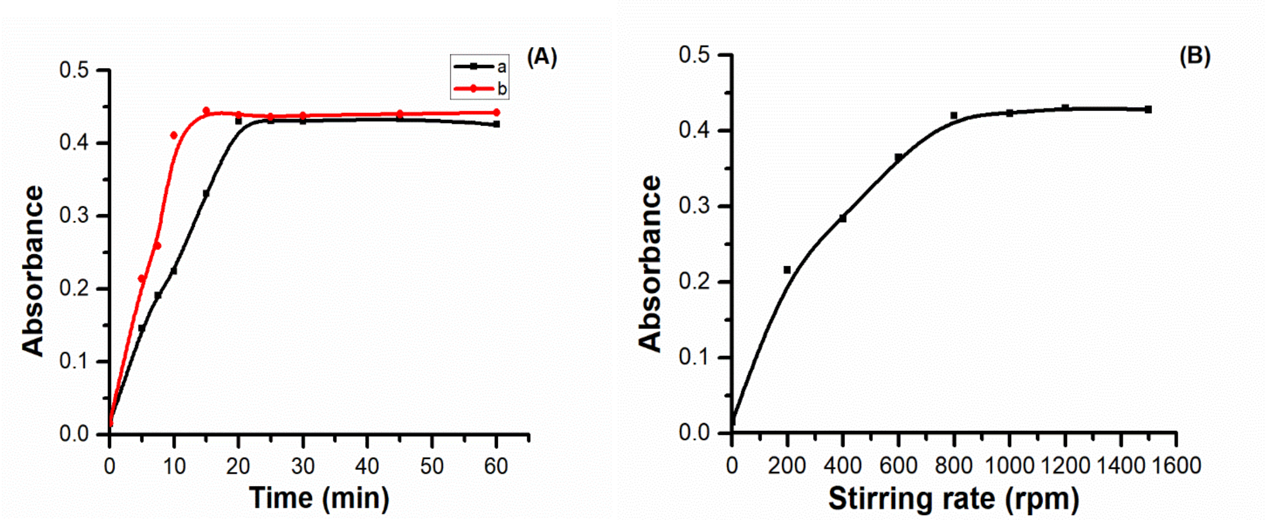

Fig. 3. Dependence of absorbance of acceptor phase on time of HS extraction for 100 (a) and 50 (b) µL of extracting phase (A) and influence of stirring rate on the extraction of iodine vapor with 1 % potassium iodide (B). Volume of acceptor phase: (A) 50 µL (a), 100 µL (b); (B) 100 µL. Concentration of nitrite: (A) 92 µg L^{-1} (a), 46 µg L^{-1} (b); (B) 92 µg L^{-1}

Effect of stirring rate. The stirring rate on a magnetic stirrer affects the entire extraction process, since the donor phase has a relatively large volume and the diffusion process in it is rather slow. Without stirring, the diffusion of iodine in the donor phase determines the overall extraction rate. It is well-known that rate of diffusion of gases in headspace is much higher than in the liquid phase. The absorbance stops to rise when the stirring rate reaches 800 rpm. After that, it remains constant. Consequently, the extraction rate now depends only on the processes occurring in the acceptor phase. To ensure that the highest possible absorbance is achieved, 1200 rpm was taken as optimal for further research.

Influence of the volumes of donor, headspace and acceptor phases on the extraction efficiency. In the three-phase system under study, two equilibria are established between the donor phase and the headspace (Eq. (2)) and also between the headspace and the acceptor phase (Eq. (3))

$$D_1 = \frac{C_G^{eq}}{C_D^{eq}} \quad (5)$$

$$D_2 = \frac{C_A^{eq}}{C_G^{eq}} \quad (6)$$

The amount of analyte absorbed by the acceptor phase, $n = C_A^{eq} V_A$, can be expressed as [25]:

$$n = \frac{C_0 V_A V_D D_1 D_2}{D_1 D_2 V_A + D_2 V_G + V_D} \quad (7)$$

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.

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 a vial with a total volume of 15 mL (Fig. 4). The absorbance of acceptor phase is directly proportional to the volume of the donor phase and is in good agreement with the values calculated by the Eq. (7). The direct dependence of absorbance vs donor phase volume indicates that the extraction percentage was almost constant under the studied conditions. 10 mL was chosen as the optimal total volume of the donor phase.

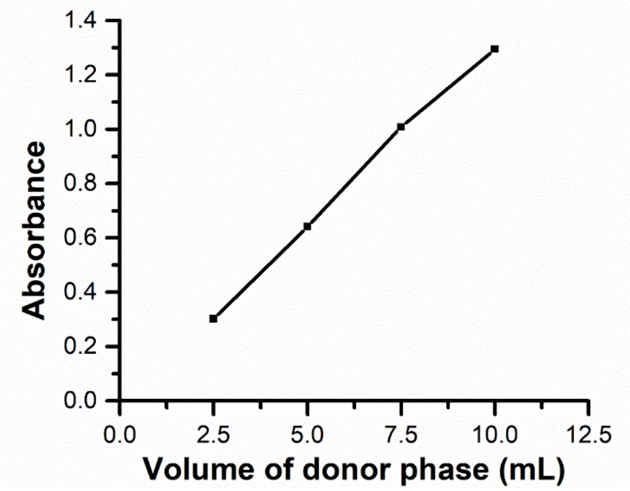

Fig. 4. Influence of volume of donor phase on the absorbance of the acceptor phase

The importance of the right choice of the headspace volume has been emphasized in previous publications [1; 2]. It was recommended to use as much as little volume of the headspace as possible. The chosen volume of vial (15 mL) met this requirement.

The volume of the acceptor phase also strongly affects the value of the analytical signal. As previously shown, the extraction efficiency is approximately the same for volumes of 50 and 100 μL. Taking into account that 50 μL is smallest possible volume of microcuvette used for measurements, it was taken as optimal to provide the highest sensitivity.

Analytical performance of the developed method. The calibration graph for the determination of nitrite ions was linear in the range of concentrations from 3 to 120 μg L^{-1} with a detection limit of 1 μg L^{-1} and a correlation coefficient of 0.9997. Equation for calibration graph was Abs = 0.00947±0.00011 C(NO_2^-), where concentration of nitrite is expressed in μg L^{-1}. The precision of the proposed method is high and amounted to 1-2% for most of the concentrations presented on the calibration graph.

Study of interference in the nitrite determination. The interfering effect of some typical ions present in natural waters on the determination of nitrite was studied. The concentration of nitrite in aqueous sample was kept constant at a level of 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^-, NO_3^- are present at least 1000-fold excess, they do not interfere with the determination of nitrite. The results obtained show that 6 mmol L^{-1} concentration of iodide did not cause any influence on the analytical signal. The concentration of NaCl 1 mol L^{-1} has no effect on nitrite determination. The most serious interference occurs when iodate or bromate is present in the sample along with nitrite. However, the results obtained showed that up to 50 μgL^{-1} of bromate and 100 μgL^{-1} of iodate can be tolerated. The concentration of bromide can reach 100 mg L^{-1}, which is higher than typically found in natural waters. It was shown that Fe^{3+} does not interfere up to 0.002 M (112 мг/л), Cr^{3+} can be tolerated up to 0.004 M (212 мг/л).

Application of the developed method to the analysis of natural waters. The developed method was applied to determine the content of nitrite in some types of natural waters. Particular attention was paid to the analysis of mine waters originating from the Krivoy Rog region. These waters are heavily contaminated with iron, chromium and many other metal ions and, in addition, contain a large amount of organic matter. The content of iron(III) was more than 0.1 M (5.6 g L^{-1}) in some cases. It was shown that when Fe^{3+} or Cr^{3+} were present in concentrations, which exceeded the allowable level, the simple separation by precipitation with diethyldithiocarbamate was efficient to remove completely such an undesired effect as well as possible effects from some other metal ions. The use of the classical method with the Griess reagent is often not sensitive enough or sometimes leads to conflicting results. Therefore, separation of nitrite ions is necessary. In the proposed hybrid method, the separation of nitrite is combined with the spectrophotometric determination. Consequently, the proposed method, as it also follows from the interference study, is highly selective and can be recommended for highly sensitive determination of nitrite ions in many types of waters.

Table 1

The results of the determination of nitrite ions in mine waters of Nord mining and processing plant (Krivoy Rog, Ukraine)

Sample	Nitrite added ($\mu g\ L^{-1}$)	Nitrite found ($\mu g\ L^{-1}$)	Recovery (%)	Total nitrite found (mg L^{-1})	Found by Griess method (mg L^{-1})
22	-	22.3±2.0	-	0.0322±0.005	<DL
	46	67.1±6.8	98.0	-	
65	-	-	-	<0.001	<DL
	96	96±1.2	100.1	-	
72	-	97.5±1.5	-	97.4±2.3	94.7±4.7
	46	150.3±5.3	104.2	-	
74	-	29.0±1.4	-	0.040±0.009	<DL
	96	119.9±4.4	96.0	-	

The content of nitrite in mine waters of the Nord mining and processing plant (Krivoy Rog, Ukraine) is less than the detection limit of the Griess method, which is accepted as standard for the analysis of natural waters. However, using the proposed method, it is possible to determine nitrite ions in most of the analyzed samples. The matrix effect of high concentrations of iron(II, III), chromium(III) as well as other metal ions is absent or can be easily removed recipitation with diethyldithiocarbamate, which follows from the recovery study.

Comparative characteristics of the developed method. Comparison of the proposed method with the reported LPME techniques for the determination of nitrite is given in Table 2. Many of the proposed methods are too time-consuming. The use of a membrane and rotatory mixer in [26] for preconcentration results in a long extraction time of 2 hours and a complicated procedure. Tedious operations, including preparation of the reaction mixture, centrifugation and cooling, are characteristic of preconcentration by micelle-mediated extraction [21]. An approach similar to that described in this paper was developed by Bendicho et al. [18]. Aqueous microdrops containing the Griess reagent, exposed in headspace, were used as an extractant for volatile nitrogen oxides formed from nitrite by direct acidification of an aqueous sample. Despite the high enrichment factor of 193 and the small volume of the acceptor phase of 3 μL, the obtained sensitivity was the same as in the method developed by us. 7 minutes of extraction is not enough to achieve complete establishment of extraction equilibrium. In addition, the percentage of extraction is significantly decreased with such a high ratio of aqueous to organic phases.

Sorption by polyurethane foam (PUF) of the reaction product between nitrite and Griess reagent and measurement of absorbance in a thin layer of PUF were used in [19] to determine nitrite and nitrate. The procedure takes more than 10 min and includes two operations – the formation of a colored substance and the sorption of it by PUF. It is inconvenient to measure the absorbance of a thin PU foam layer. This technique, which enhanced analytical sensitivity of colorimetric solution methods, has several shortcomings. It is extremely time and labor consuming since several steps are required, including preparation of sorbent, reaction development, filtration, washing, loading of the cell with the particles, detection and unloading for each determination. Furthermore, skill and expertise are required to form a homogeneous solid layer in the cell as well as the use of large volume of sample solution and a large amount of solid material that is renewed after detection. Finally, classical ion-exchangers exhibit kinetic problems associated with diffusional transport of analyte.

Ion pair-based dispersive liquid-liquid microextraction was used to preconcentrate iodine formed in the reaction between nitrite and iodide [27]. The method has similar sensitivity to that proposed in this study, although the extraction efficiency of the direct approach is about ten times better than for the HS mode of LPME. Solvent stir bar microextraction technique with three-hollow fiber configuration was proposed for the determination of nitrite in river water [28]. The method is complex. For determination, three pieces of hollow fiber with a diameter of 4.4 cm are used, which, before determination, should be immersed for 1 min in an organic solvent (n-octanol), and then the open ends of the fibers are thermally closed. The total time of determination is long, taking into account 20 min required to finish the reaction between nitrite and iodide, 8 min of extraction and time necessary to accomplish all the necessary operations.

Vortex-assisted liquid-phase microextraction based on supramolecular solvent was used to determine nitrite in meat [29]. However, the method has bad sensitivity, which is explained by the fact that a poorly absorbing form was used (intrinsic absorption of nitrite ion) in the determination. The volume ratio of the donor (2 mL) and acceptor phases (0.4 mL) was also low. Therefore, it is not clear how such a high preconcentration factor (PF = 95) was declared in the article. A hydrophobic deep eutectic solvent was used as an extrahent in vortex-assisted dispersive liquid-liquid microextraction in combination with HPLC for the determination of nitrite in water [14]. Procedure is somewhat complicated, as it involves several stages, such as the formation of a colored substance, the synthesis of a deep eutectic solvent, extraction and centrifugation. An expensive instrument (HPLC) was used for the nitrite detection. A large volume of extrahent (8 mL of 5% Triton X-100) was used for the cloud point extraction of iodine formed in the reaction of nitrite with iodide, which limits the preconcentrating achieved in the method [22]. The CPE extraction takes a long time more than 30 min to complete the separation. The same can be said about another method, in which the formation of an ion associate between nitrite and 2,6-bis(4-methoxyphenyl)-4-phenyl pyrylium was used for its extraction with microcrystalline naphthalene [30]. A large volume of extracting solvent was used (5 mL of 20% naphthalene) was used, which deteriorated the obtained sensitivity.

The reaction product of nitrite with 2,3-diaminonaphthalene was extracted using a dispersive LLME [31 Zahedi]. The method is a multi-step procedure with moderate sensitivity. Vortex-assisted LLME using isooctanol as extractant followed by spectrophotometry was developed for the extraction and determination of trace amounts of nitrite in water samples [32]. The method is based on a selective ion-pair complex of triiodide with Malachite Green. This method has a low enrichment factor and also uses large volumes of sample (up to 40 mL) and organic solvent (2 mL).

Conclusions

A new highly selective, sensitive, and low-cost spectrophotometric procedure for the determination of nitrite was developed and applied to the analysis of mine waters. Preconcentration was carried out using a new recently proposed approach based on headspace microextraction. HS-LPME is clearly different from other LPME methods. This approach allows the analyte to be easily and completely separated from complex matrices. In the HS-LPME, phase separation and following transfer to the instrument are greatly simplified. Unlike other types of LPME [4; 6; 33; 34], both water-immiscible and water-miscible solvents can be used to extract the analyte from the donor phase. Application of HS-LPME is limited to volatile or semi-volatile analytes.

Table 2

Comparison of the proposed method with reported LPME techniques for the determination of nitrite

Technique	Method	LOD (μg L⁻¹)	Linear range (μg L⁻¹)	RSD (%)	Extraction time, min	Sample volume (mL)	Volume of extracting solvent, μL	Ref
Membrane-assisted LPME - UV–vis	Condensation with aniline and N-(1-naphthyl)ethylenediamine, extraction with 150 μL of 1 M HCl through PTFE membrane filled with n-decane	0.15	0.5-50	<10%	120	10	150	[26]
CPE - UV–vis	CPE with Triton X-100 after reaction of nitrite with p-nitroaniline in the presence of diphenylamine	0.87	2–40	2.6	~20	5	500	[21]
HS SDME - UV–vis	Acidification of aqueous sample and sorption with Griess reagent	1.5	20–3000	3–10	7	10	3	[18]
SP spectrophotometry	Sorption of the dye formed in Griess reaction with 2 mm thick polyurethane foam	5	5–140	1	1 + 10	100	1×3.5×0.2 mm	[19]
UV—vis after dispersive LLME	Reaction of nitrite with iodide to form triiodide, extraction into CCl_4 using trioctylmethylammonium	0.4	5–300	0.7–1.6	10+5	5-8	200	[27]
Solvent stir bar ME with three-hollow fibers	Reaction of nitrite with iodide to form triiodide, extraction into n-octanol using tetrabutylammonium chloride	1.6	5–1000	4	20+8	35	50	[28]
VA -based LPME	Extraction with supramolecular solvent (decanoic acid (20 mg) and tetrahydrofuran (400 μL))	35	100–300000	9.6	2+2	2	400	[29]
VALLME	Reaction with nitrite, formation of ion associate of J_3^- with Malachite Green and extraction into isooctanol	0.5	1–100	2–4	20 sec	10-20	2000	[32]
DLLME-SFOD	Derivatization with 2,3-diaminonaphtalene, extraction with 1-dodecanol	94	100–1100	5	>15	10	250	[31]
Extraction by naphthalene	Reaction with 2,6-bis(4-methoxyphenyl)-4-phenyl pyrylium and extraction by 20% naphthalene	10	15–135	2.1		250	5 mL	[30]
CPE	Reaction of nitrite with iodide and CPE of triodide with Triton X-100	6	8–120	3.4	>30	7	8 mL SAS	[22]
VA-DLLME	Diazotization-coupling reaction of nitrite with p-nitroaniline and diphenylamine, ME with hydrophobic deep eutectic solvent	0.2	1–300	4–6		5	150	[14]
IV-HS-LPME	Acidification of aqueous sample and sorption with 1% KI	1.0	3–120	1–2	17	7.75	50 μL of 1% KI	This work

* LPME – liquid phase ME; HS SDME – headspace single drop ME; VA-DLLME – vortex-assisted -dispersive liquid-liquid ME; CPE – cloud point extraction; SFOD – solidified floating

This approach combines several steps in sample handling, including separation, preconcentration, and transfer of the extract to the instrument. However, it suffers from several factors that cause significant worsening of reproducibility. The microdrop can increase or decrease in volume due to the absorption of water vapor or evaporation of the solvent, respectively. Equilibrium is often not achieved in procedures using the HS-LPME, as the microdrop can become unstable with longer extraction times. The solvent can separate from the tip of the needle, so the experiment requires careful and complex manual operation. Holding the microdrop at the tip of a microsyringe needle makes the preconcentration method incompatible with a number of commonly used detection methods, including spectrophotometry, luminescence, or flame AAS.

The proposed method completely eliminates most of the disadvantages inherent to the previous approaches, including too small volume of the extraction phase or problems with the stability of microdrop, and restrictions on the stirring speed or extraction time. Compared to previous approaches, IV-HS-LPME method is fully compatible with conventional instruments and accessories used in spectrophotometry. It has a higher extraction efficiency compared to the approach using the suspended microdrop. The method is distinguished by very good reproducibility, since the optimal parameters are chosen under conditions in which complete equilibrium is established. As a result, a simple model of interfacial equilibria is applicable to describe the data obtained.

Volatile products were obtained in the reaction of nitrite with an excess of iodide. Vapors of iodine were absorbed by 1% potassium iodide to form a highly absorbing triiodide complex. The absorbance of triiodide was measured in a 50 µL microcuvette.

An aqueous solution of potassium iodide was used for the preconcentration of nitrite, and thus extraction with a toxic solvent was avoided. Comparison of the proposed method with the previously reported methods for preconcentration and spectrophotometric determination of nitrite (Table 2) shows that the proposed method is faster and simpler than existing methods and provides a wider dynamic range and lower detection limit than most existing procedures.

The proposed method is of advantage for the determination of nitrite in mine waters. The sensitivity of the method is much higher than of the standard Griess method. In addition, interference from large amounts of iron(II, III), chromium(III) and other metal ions is significantly lower. The color of turbidity of the sample do not affect the determination of nitrite.

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