



A novel vortex-assisted liquid–liquid microextraction approach using auxiliary solvent: Determination of iodide in mineral water samples

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ABSTRACT

A novel vortex-assisted liquid–liquid microextraction (VA–LLME) for determination of iodide was developed. The method includes the oxidation of iodide with iodate in the presence of hydrochloric acid followed by VA–LLME of the ion-pair formed between ICl_2^- and Astra Phloxine reagent (AP) and subsequent absorbance measurement at 555 nm. The appropriate experimental conditions were investigated and found to be: 5 mL of sample, 0.27 mol L^{-1} HCl, $0.027 \text{ mmol L}^{-1}$ KIO_3 as the oxidation agent, 250 μL of extraction mixture containing amyl acetate as the extraction solvent and carbon tetrachloride as the auxiliary solvent (1:1, v/v), 0.04 mmol L^{-1} AP reagent, vortex time: 20 s at 3000 rpm, centrifugation: 4 min at 3000 rpm. The calibration plot was linear in the range 16.9–169 $\mu\text{g L}^{-1}$ of iodide, with a correlation coefficient (R^2) of 0.996, and the relative standard deviation ranged from 1.9 to 5.7%. The limit of detection (LOD) and limit of quantification (LOQ) were 1.75 and 6.01 $\mu\text{g L}^{-1}$ of iodide, respectively. The suggested procedure was applied for determination of iodide in real mineral water samples.

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1. Introduction

Iodine is an essential micronutrient element. It is required for the synthesis of two thyroid hormones, thyroxine and tri-iodothyronine, which are necessary for the control of cellular metabolism, growth, development of body structures and neuronal function and development. The human body cannot synthesize iodine; it is therefore necessary to obtain it from different sources, with food being the most important of these. Iodine deficiency during pregnancy and infancy may result in irreversible brain damage, impair growth and neurodevelopment of offspring and increase infant mortality [1,2]. Globally, an estimated 740 million people are affected by iodine deficiency disorders (IDD), and more than 2 billion are thought to be at risk of IDD. Elevated quantities of iodine can also be harmful to health.

Iodine is a widespread trace element in the earth's crust and hydrosphere [3,4]. Seawater in particular is a huge reservoir of iodine. As is well known, iodine is an electronegative element with various oxidation states (−1, 0, +1, +3, +5 and +7) [5] and it exists in different chemical forms in aqueous solution. Iodine is a redox-sensitive element and is present in a wide variety of inorganic and organic compounds, the most common inorganic forms being I^- (iodide), HOI (hypoiodous acid), I_2 (elemental iodine), and IO_3^- (iodate). Speciation of iodine in natural water depends on several parameters, including water chemistry, pH, Eh, temperature and rate of generation of biomass in an ecosystem [4].

The halides concentration in water samples can be an important parameter in determining water quality. The iodide content of drinking water is sometimes checked to decide the amount of supplementation needed [5]. Therefore, the determination of halides, including iodide, in different kinds of water samples is an important analytical task.

Several methods can be used to determine iodide ions in various samples, including capillary electrophoresis [6,7], voltammetry [8,9], gas-chromatography, ion-chromatography and high performance liquid chromatography [10–13], as well as kinetic methods [14,15]. However, spectrophotometric (SP) methods have been among the most frequently used up to the present. One of the most commonly used SP methods is based on the chemical oxidation of iodide and the direct measurement of absorbance [16] near the ultraviolet region or in the visible region after the addition of starch reagent [17]. Extraction of ion pairs of iodide or other iodine forms with bulky cations is a promising way to enhance the sensitivity and selectivity of SP determination. Different approaches have been proposed, including the extraction of ion associates of iodine forms with basic organic dyes, such as Rhodamine B (as RB-ICl_2^- ion pair) [18], Methylene Blue [19] or Brilliant Green [20] (as MB or BG-iodide ion pair), the extraction of ion pairs of periodate with colorless organic cations like, for example, tetramethylammonium iodide [21] or amiloride [22].

Solvent extraction, or in other words liquid–liquid extraction (LLE), is one of the oldest extraction techniques and the one that is

used most frequently in aqueous samples with complex matrix composition. Recently, various miniaturized extraction methodologies have been developed and have become very popular among researchers, as evidenced by the continually growing number of original papers and reviews devoted to them [23–31]. Dispersive liquid–liquid microextraction (DLLME), developed by Rezaee in 2006 [32], is currently receiving a great deal of interest from analytical chemists [33]. The main drawbacks of DLLME result from (a) the requirement that the extraction solvent has a density higher than that of water for simple phase separation; (b) the necessity of centrifugation, which is a time-consuming step; and (c) the need to use a dispersive solvent.

Various solutions have been reported that enable the application of solvents with a density lower than that of water; these include, for example, the application of various special devices [34–36] or the application of an auxiliary solvent to adjust the extraction phase density, as previously reported by our lab [37]. Very recently Hassanpoor et al. reported an auxiliary solvent demulsification microextraction [38]. Application of a dispersive solvent can lead to a decrease in the partition coefficient of analytes in the extractant solvent [39]. Both vortex-assisted liquid–liquid microextraction (VA–LLME) and ultrasound-assisted emulsification–microextraction (USAEME) can be considered as alternatives to conventional DLLME; they have the advantages of the above-mentioned method but in contrast do not require a dispersive solvent [40]. VA–LLME has been used mainly for determination of organic analytes and only to a lesser extent for determination of inorganic analytes. To the best of our knowledge, the method has not previously been applied for the determination of an inorganic anion.

In the present work, we report a novel VA–LLME method for determination of iodide. The method is based on the oxidation of iodide with iodate in the presence of hydrochloric acid, followed by VA–LLME of the ion-pair formed between ICl_2^- with polymethine dye Astra Phloxine into an organic phase, with subsequent spectrophotometric quantification. This is, as far as we know, the first time an auxiliary solvent (carbon tetrachloride) has been used for adjusting the density of the extraction phase in the VA–LLME method in order to determine an inorganic anion. The developed method was applied for the determination of iodide in real mineral water samples.

2. Experimental

2.1. Chemical and reagents

All chemicals and solvents used were of analytical reagent grade. The 2 mol L^{-1} HCl was prepared by dilution of concentrated hydrochloric acid (Sigma Aldrich, Germany). The 1 mmol L^{-1} Astra Phloxine FF (AP) was prepared by dissolving 196.5 mg of the reagent in a few milliliters of ethanol and subsequent dilution with water up to a volume of 500 mL. The 0.01 mol L^{-1} iodide stock solution was prepared by dissolving 166 mg of KI (ITES, Slovakia) in 100 mL of water. The $10 \mu\text{mol L}^{-1}$ iodide working solution was prepared daily by dilution of the stock solution. The 0.01 mol L^{-1} solution of iodate was prepared by dissolution of the respective amount of KIO_3 (Erba Lachema, Slovakia) in water. Both the iodate and iodide solutions were stored in amber coloured glass flasks in a dark place.

The carbon tetrachloride, chloroform, benzene, toluene, ethyl acetate and *n*-butyl acetate used were all purchased from ITES (Slovakia), the *n*-amyl acetate from Merck (Germany), and the octanol from Sigma Aldrich (Japan).

2.2. Apparatus

A SPECORD S 600 UV–vis spectrophotometer (Analytik Jena, Germany) with glass cells of path length 2 mm was used for absorbance measurements. A UCI-150 ultrasonic cleaning bath (RAYPA, Spain) equipped with a high frequency generator (325 W power and 35 kHz frequency) was used to remove CO_2 bubbles from the water samples. A VM-3000MD vortex mixer (Medline Scientific, UK) was used to assist the extraction process, and centrifugation was performed with a CN-2060 centrifuge (MRC, Israel).

2.3. Sample collection

The mineral water samples, bottled in glass, were purchased from a local supermarket in Slovakia and stored at room temperature before use. Once opened, they were stored at 4°C and analyzed within 3 days. Before analysis, the mineral water sample was degassed in an ultrasonic bath for 20 min.

2.4. VA–LLME procedure

For the VA–LLME, 1 mL of 2 mol L^{-1} hydrochloric acid, 5 mL of a water sample containing from 0.127 to $1.27 \mu\text{g}$ of iodide and 0.2 mL of 1 mmol L^{-1} KIO_3 were placed into a 15 mL screw cap glass tube with a conical bottom, and the volume was filled up to 7.2 mL with water and thoroughly mixed. Then 250 μL of a solvents mixture containing amyl acetate as the extraction solvent and carbon tetrachloride as the auxiliary solvent (1:1, v/v) and 0.3 mL 1 mmol L^{-1} AP were added to the sample solution. The tube was capped immediately and the mixture was shaken on a vortex agitator at 3000 rpm for 20 s. A cloudy solution was formed and the ion associate containing I_2Cl^- and AP reagent was extracted into the fine droplets of organic solvent. After a 4 min delay, the tube was centrifuged at 3000 rpm for 4 min. The sedimented phase was withdrawn using an automatic pipette and transferred to a glass cell with 2 mm path length; the absorbance was then measured at 555 nm.

3. Results and discussion

3.1. Reaction mechanism

The method is based on the oxidation of iodide by iodate in the presence of hydrochloric acid with the formation of ICl_2^- anion (Reaction 1) and subsequent VA–LLME of the ion association complex of ICl_2^- with AP. The present method involves the oxidation of iodide to ICl in the excess of iodate and hydrochloric acid and the formation of ICl_2^- due to the small equilibrium constant for its decomposition: (Reaction 2) [41].



The proposed scheme of the reaction was confirmed by the measurement of the absorption spectrum of the studied system in the conditions of the proposed method without addition of the dye (Fig. 1). The obtained value of the absorbance is in close correspondence with complete formation of ICl_2^- anion ($\epsilon = 243 \text{ mol}^{-1} \times \text{L} \times \text{cm}^{-1}$ at $\lambda_{\text{max}} = 343 \text{ nm}$) [41]. The bands of I_2Cl^- at 437 nm ($\epsilon = 1100 \text{ mol}^{-1} \times \text{L} \times \text{cm}^{-1}$) [41], I_3^- at 288 nm ($\epsilon = 38790 \text{ mol}^{-1} \times \text{L} \times \text{cm}^{-1}$) and 350 nm ($\epsilon = 25750 \text{ mol}^{-1} \times \text{L} \times \text{cm}^{-1}$) [42] or I_2 at 460 nm ($\epsilon = 730 \text{ mol}^{-1} \times \text{L} \times \text{cm}^{-1}$) [41] are absent in the obtained spectrum.

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