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Comparison of two novel in-syringe dispersive liquid–liquid microextraction techniques for the determination of iodide in water samples using spectrophotometry

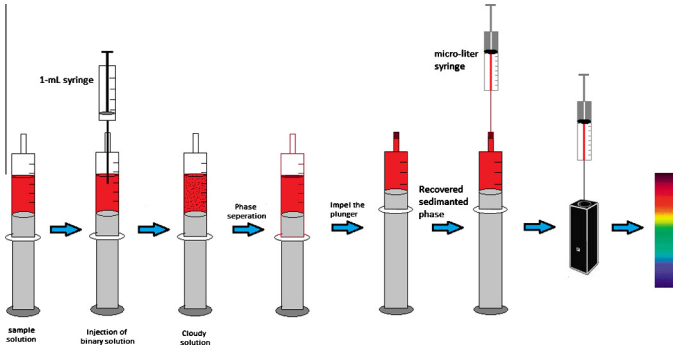
Massoud Kaykhaii *, Mona Sargazi

Department of Chemistry, Faculty of Sciences, University of Sistan and Baluchestan, Zahedan 98135-674, Iran

HIGHLIGHTS

- The first report of dispersive liquid–liquid microextraction for an anionic species.
- Trace levels of iodide was determined spectrophotometrically in water samples.
- Advantages: simple, rapid, low sample volume, economical, high enrichment factor.
- Be useful in less developed area with no access to advanced analytical instruments.

GRAPHICAL ABSTRACT



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ABSTRACT

Two new, rapid methodologies have been developed and applied successfully for the determination of trace levels of iodide in real water samples. Both techniques are based on a combination of in-syringe dispersive liquid–liquid microextraction (IS-DLLME) and micro-volume UV–Vis spectrophotometry. In the first technique, iodide is oxidized with nitrous acid to the colorless anion of ICl_2^- at high concentration of hydrochloric acid. Rhodamine B is added and by means of one step IS-DLLME, the ion-pair formed was extracted into toluene and measured spectrophotometrically. Acetone is used as dispersive solvent. The second method is based on the IS-DLLME microextraction of iodide as iodide/1, 10-phenanthroline-iron$^{(II)}$ chelate cation ion-pair (colored) into nitrobenzene. Methanol was selected as dispersive solvent. Optimal conditions for iodide extraction were determined for both approaches. Methods are compared in terms of analytical parameters such as precision, accuracy, speed and limit of detection. Both methods were successfully applied to determining iodide in tap and river water samples.

Introduction

Iodine is an essential element of human nutrition. Nearly one third of the global population has insufficient iodine intake and are at risk of developing iodine deficiency disorders which causes symptoms such as cretinism, goiter, irreversible mental retardation and development of anomalies. Most countries have iodine supplementation and monitoring programs. World Health Organization (WHO) recommends the daily intake of 150 μg of iodine for adults and 200 μg for pregnant and lactating women [1]. On the other hand, an excess of iodine is also harmful to health, both iodine deficiency and excess have been associated with the development of goiter.

Several advanced methods have been proposed for the quantitative determination of iodide ions which are reviewed in several recently published review articles [2–4]; among them spectrophotometric methods are the most common to date [5]. That's mainly

* Corresponding author. Tel.: +98 541 2446413; fax: +98 541 2446888.
E-mail address: kaykhaii@chem.usb.ac.ir (M. Kaykhaii).

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because the techniques which avoid problems to destroy potential interfering substances, such as neutron activation analysis or inductively coupled plasma-mass spectroscopy, are unrealistic for widespread use, because of high cost, large sized and degree of sophistication [6]. On the other hand, the conventional UV–Vis spectrophotometry methods of iodide detection suffer from serious poor sensitivity [7] and they are very time consuming, for example, the most commonly used laboratory method for analyzing urinary iodine concentration which is based on Sandell–Kolthoff reaction [8], takes 3 days for one assay run [6]. However it is a very widely used detection method mainly because of its low cost and simplicity of use. If coupled with some advanced preconcentration techniques, the analytical performance of spectrophotometry could be significantly improved. This would greatly expand its applications, especially for the less developed area without more advanced analytical instruments.

In the present study, a new dispersive liquid–liquid microextraction technique without centrifugation was investigated as a sample pre-treatment method for spectrophotometric analysis of iodide. This novel extraction technique, first reported in 2009 [9], named in-syringe dispersive liquid–liquid microextraction (IS-DLLME), is of rapidly increasing interest [10–15]. Its simplicity and fastness are probably the most attractive benefits of this technique. A 5 or 10-mL glass syringe is used as an extraction, separation and preconcentration container. By means of a 1-mL syringe fitted onto the tip of this syringe rapid injection of a solvent mixture into the aqueous sample is done by which one component of the solvent dissolves nearly instantaneously (i.e., the dispersive solvent) while the second component (i.e., the extraction solvent) remains and is disrupted into a cloud of fine droplets. The simultaneous enormous increase of the interaction surface with the sample enables efficient mass transfer of the analyte into the extraction solvent droplets. After separation of two phases, the extractant containing the target analytes can be easily collected and transferred into the analytical instrument for analysis. Collection of the droplets, which is generally done in DLLME by centrifugation, is not necessary in this technique.

This paper presents two modern, simple and efficient methods for preconcentration and separation of iodide from water and samples employing in-syringe dispersive liquid–liquid microextraction. In both approaches iodide is micro-extracted as an ion-pair species into an organic phase followed by spectrophotometric determination. The effects of various experimental parameters on the extraction were investigated for each method and operating conditions were also optimized. Both approaches showed satisfactory sensitivity and detection limits.

Experimental

Instrument

A Shimadzu UV/VIS spectrophotometer, Model UV-160 (Kyoto, Japan) was used for measuring the absorbance and recording the spectra. This instrument was equipped with two 10 μL microcells (Agilent, USA; part number 5063-6565). A Metrohm (Switzerland) model EasySeven pH meter was used for pH measurements.

Reagents

All reagents were of analytical grade and were purchased from Merck (Germany) and used as received. Milli-Q® water (18.3 M Ω cm) was used throughout the experiment after filtering through 0.22 μm Nylon membrane. Weigh in 1.3081 g KI (superior grade) and dissolve the whole amount with 1000 mL water to obtain 1000 mg L^{-1} iodide solution. Working standard solutions were prepared by serial dilutions of this solution prior to analysis. Rhodamine B (0.02 M), sodium nitrite (0.01 M) and 1,10-phenanthroline (2.4×10^{-2} M) were prepared by dissolving appropriate amounts of solid in doubly distilled water. 5×10^{-3} M solution of ferrous ammonium sulfate was prepared by dissolving 0.3731 g of the solid in dilute sulfuric acid. Phosphate buffer (1 M) was prepared with potassium di-hydrogen phosphate and sodium mono hydrogen phosphate and used for pH adjustments, using sodium hydroxide or sulfuric acid. A solution of 4×10^{-3} M tris(1,10-phenanthroline)iron(II) sulfate was prepared with ferrous ammonium sulfate and 1, 10-phenanthroline. Nitrobenzene which was used for chelate extraction was purified by vacuum distillation. Before extraction, it was saturated with distilled water and after extraction; it was dried using anhydrous sodium sulfate.

In-syringe dispersive liquid–liquid microextraction procedures

Method 1

An aliquot of 3.0 mL aqueous sample containing iodide was placed in a conventional 10-mL glass syringe. A mixture of 500 μL sodium nitrite (0.01 M), 500 μL rhodamine B (0.02 M) and 3.10 mL concentrated hydrochloric acid (12.1 M) was added and then the mixture was diluted with doubly distilled water to the volume of 7.5 mL. This adjusts HCl concentration to 5 M in the final solution. By means of a 1-mL syringe, 175 μL of extraction solvent (toluene) and 700 μL dispersive solvent (acetone) was injected rapidly into the sample solution through the tip of 10 mL syringe. An emulsion (water, extraction solvent, and dispersive solvent) was formed in this syringe immediately. The mixture was gently shaken. After about 5 min, separation of the two phases was achieved. Later, the plunger of the syringe was slowly moved toward its tip allowing the full recovery of the extracting phase. A pipette tip was fitted onto the tip of the syringe and the plunger of syringe was promoted to move the floated extractant into the pipette tip. Hence, the extractant containing the target analyte was easily collected and withdrawn by a microsyringe and 10 μL was transferred into UV–Vis spectrophotometer for analysis.

The reaction between iodide and nitrous acid in 5 M hydrochloric acid is [16]:

$$I^- + 2HNO_2 + 2H^+ + Cl^- \rightarrow ICl + 2NO + 2H_2O$$

In this medium, iodine chloride reacts further with chloride to produce ICl_2^-, which has a formation constant of 170. This anion is extracted into toluene as the ion-pair with rhodamine B. Fig. 1a shows the chemical structure of this ion pair which has a maximum wavelength of absorption at 562 nm.

Method 2

This extraction is based on the ion-pair formation between I^- and $Fe(phen)_3^{2+}$ which can be easily extracted into nitrobenzene phase [17].

500 μL of a sample solution containing iodide was placed in a conventional 10-mL glass syringe. Using phosphate buffer, mixture was diluted to 5 mL and 1 mL of 4×10^{-3} M tris(1,10-phenanthroline)iron(II) sulfate was added to it. After then, by means of a 1-mL syringe, a mixture of 150 μL nitrobenzene (saturated with water) and 250 μL of methanol (dispersive solvent) was sprayed rapidly into the sample solution through the tip of 10 mL syringe. A cloudy solution formed immediately. The mixture was gently shaken. After about 5 min, separation of the two phases was achieved. Later on, the plunger of the 10 mL-syringe was slowly moved to the initial point allowing the recovery of the nitrobenzene phase from the wall and the lower part of the syringe while the aqueous sample was removed from the unit. The extracting phase containing the target analyte was easily recovered from the syringe tip and