



A miniaturized analyzer for the catalytic determination of iodide in seawater and pharmaceutical samples

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ARTICLE INFO

Article history:

Received 12 December 2012

Received in revised form

22 February 2013

Accepted 28 February 2013

Available online 13 March 2013

Keywords:

Iodide

Air-bubble removal

Kinetic determination

Flow conduit

Multisyringe flow injection analysis

ABSTRACT

A monolithic flow conduit was especially designed and coupled to a multisyringe unit (MSFIA) in order to develop a kinetic analytical method. The new device, denoted CHIP, integrates different functions in a reduced size including confluent mixing, reaction coil, and thermostating, which allowed minimizing the dimensions of the entire analyzer system. The CHIP–MSFIA was satisfactorily applied to the determination of iodide using the Sandell–Kolthoff reaction. The resulting system allows fast, simple and automatic analysis in seawater samples and a pharmaceutical preparation. By the use of an additional syringe, reagent blank, sample blank, unspecific interferences, and sample analyte concentration was evaluated by simply changing the mode of operation. The instrumentation and analytical procedures were optimized in respect of sensitivity. A limit of detection of $4.7 \mu\text{g L}^{-1}$ and linear working range of $4.3\text{--}70 \mu\text{g L}^{-1}$ were achieved.

Two new modes of air bubble elimination were developed and employed in this work, leading to improved reproducibility (RSD % = 1.5%) and method robustness. The accuracy of analysis for seawater samples was evaluated by an Add–Recovery test obtaining recoveries between 97 and 106%. For the quantification of iodide in the pharmaceutical sample, standard addition calibration was required. No significant differences between the found and the certified value were found. The entire analytical procedure lasted about 150 s enabling a measuring frequency of 23 h^{-1} .

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1. Introduction

Analytical flow techniques (FT), extensively described in distinct reviews [1–3] and monographs [4–6] are the most adequate systems for the automation of the analytical methods. Main advantages such as simplicity, efficient use of reagents and sample, and versatility, i.e. flexibility and applicability to the automation of a multitude of sample preparative procedures, detection techniques and analytes have been proven by a number of publications, which recently surpassed 20,000 [7].

One important analytical application where FT surely stands out from other approaches is kinetic determination. This is because reproducible metering and mixing of all solutions, precise timing until data readout, and shielding of the reaction mixture from outer contamination are imperative requirements, which can be perfectly fulfilled using FT. Software-configurable FT operations are possible in Sequential Injection Analysis (SIA) [8,9] or in Multisyringe Flow Injection Analysis (MSFIA) [1,10] even

allows the adaptation of the reaction conditions e.g. reaction time, sample volume, or operation scheme.

Under such strict control of the reaction's conditions, evaluation of a reaction's kinetic bears the potential of highly sensitive determination of catalyzing species. However, the most critical factor in such approaches is probably the reaction temperature, affecting (1) the reaction kinetic, (2) the viscosity of the solutions and by this the mixing conditions, (3) the gas solubility of the solutions, and (4) the refraction index of the solution, which can affect applying optical detection methods.

In this work, a monolithic flow conduit made of PMMA, following denoted CHIP was especially designed for kinetic determinations using a multisyringe pumping unit for solution handling leading to a robust and simple MSFI-Analyzer. Monolithic flow conduits have been former reported as the possibility to integrate different functions in one single and purpose-made flow devices [11–14] which finally has led to the multi-purpose monolithic conduit known as Lab-on-Valve (LOV) [3,15].

The objective of the presented work was the development of a miniaturized analyzer system by reducing manifold dimensions, improvement the robustness of the manifold configuration and the mixing efficiency of the implied reagents, and, in particular, by strict temperature control of the integrated reaction coil.

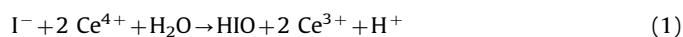
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MSFIA can be considered as an ideal choice for the solution propelling in kinetic measurements since it offers the possibility of simultaneous propulsion of up to four different solutions, e.g. sample and reagents, in a smooth, homogeneous, and pulse-less flow mixed in constant ratio. Further characteristics is the individual activation or de-activation of each pumping channel (multi-commutation) and operation over a wide, computer-controlled and reliable flow rate range without affected by neither flow resistance nor sample viscosity. This allows homogeneous and highly reproducible mixing of the implied solutions, an imperative requirement for kinetic determinations. Multi-commutation is of special interest for improving the methods of performance. It allows flow stop operations and minimizes the reagent consumption by zone-merging of sample and reagent instead of continuous confluence of the reagent to the carrier flow.

In addition to the CHIP design, we propose two simple approaches for partial reagent and carrier degassing, air bubble removal and decreased air bubble stacking which improved greatly the robustness of the analyzer operation.

To prove the usefulness of the combination of MSFIA with the designed CHIP, the system was applied to the kinetic determination of iodide using the Sandell–Kolthoff reaction [16] with the Ce(IV) reduction followed by spectrophotometric detection. In 1934, Sandell and Kolthoff described the catalytic effect of iodide on the Redox-reaction between Ce(IV) and As(III). Later, Stanley and Thomas [17] proposed a complex reaction mechanism indicating that only iodide itself but not iodine catalyses the oxidation of As(III) to As(V) and that acidity of the reaction mixture would increase. Although the mechanism of the reaction seems to be not well established yet, it is an accepted standard reaction for the determination of iodide and has been widely applied to different samples due to its high sensitivity and selectivity [18,19].



Iodine is an essential element for the human health as is a part of the thyroid hormones participating in the regulation process of the cell metabolism. It shows similar importance for numerous biological systems [20–22]. As nutrient additive, it is gained especially from macro-algae. Iodine is present in low concentrations in soils and is also found in seawater in concentration in order of 50 ppb in the mixed ocean surface layer, expressed as total iodine, i.e. iodide and iodate.[19,23]. Monitoring of iodide concentration in different kinds of samples including pharmaceutical preparations and dietetic complements [24,25], biological fluids [22,26,27], seawater [20,28], drinking water [29] has an increasing attention.

A variety of analytical methodologies have been proposed for iodide determination, including manual [24,30], automated [15,19,23,25,26] and chromatographic methods [19,27]. Used detection techniques included voltamperometry [27], potentiometry with ion-selective electrodes [31], thermometry [26], ICP-MS [18], chemiluminescence [22], ion chromatography [32,33] capillary electrophoresis [34], and most widely used, spectrophotometry [16,18,19,22,26,28,29]; based on the Sandell–Kolthoff reaction to a significant percentage. For more details, the reader is referred to an IUPAC report [19] and an extensive review article on this topic [18]. However, none of these studies have resulted in a portable system able to perform on-board iodide measurement. In this sense, the proposed analyzer offers the potential of in field application of iodide monitoring. Considering the toxicity of the required reagents for the Sandell–Kolthoff reaction but the common use as reference of this method, it is obvious that miniaturization of the manual method with the aim of a simpler, less expensive, and minimal consumption of the reagents is

appealing. Further requirements such as accurateness, rapidness, and automation are evident.

2. Materials and methods

2.1. Reagents and standards

Purified milliQ water was used throughout for preparation of all the solutions. For the preparation of analytical standards, 0.131 g of potassium iodide, previously dried at 110 °C, were precisely weighed and dissolved in 100 mL of milliQ water obtaining a 1.001 g L⁻¹ iodide stock solution. Working standards were prepared by successive dilutions of the stock solution.

Stock solutions of 5 mol L⁻¹ sulfuric acid and 5 mol L⁻¹ nitric acid were prepared by appropriate dilution of commercial concentrated acids of analytical reagent grade purity. Acidic reagent solutions of Ce(IV) and As(III) were prepared daily by appropriate weighing of (NH₄)₄Ce(SO₄)₄ · 2 H₂O and NaAsO₂ in diluted sulfuric or nitric acids and kept in dark until used. Optimized composition of the reagents were 3.5 mmol L⁻¹ of Ce(IV) and 10 mmol L⁻¹ of As(III) in each 0.27 mol L⁻¹ sulfuric acid.

Synthetic seawater (SSW) was prepared according to the recommendations given elsewhere [30] by dissolving the following components in milliQ water with given final concentrations: 3.0 mg L⁻¹ NaF, 20 mg L⁻¹ SrCl₂ · 6H₂O, 30 mg L⁻¹ H₃BO₃, 100 mg L⁻¹ KBr, 700 mg L⁻¹ KCl, 1470 mg L⁻¹ CaCl₂ · 2H₂O, 4000 mg L⁻¹ Na₂SO₄, 10.8 mg L⁻¹ MgCl₂ · 6 H₂O, 23.5 mg L⁻¹ NaCl, 20.0 mg L⁻¹ Na₂SiO₃ · 9H₂O, and 200 mg L⁻¹ NaHCO₃. All given reagents were purchased from Scharlau SA (Barcelona, Spain).

A 5 wt % solution of Nafion perfluorinated ion exchange resin in lower aliphatic alcohols was purchased from Sigma Aldrich (CITY, Germany) and used for PTFE coating as described in Section 3.2.

A solution of 0.5 mg L⁻¹ indigo carmine Panreac SA, (Barcelona, Spain) was used as visualization aid to adjust the operational volumes and to observe the flow pattern in the CHIP.

2.2. Flow conduit chip

The CHIP, shown schematically in Fig. 1, was especially made of three PMMA pieces of 85 × 44 × 10 mm. Throat holes for UNF ¼" 28 fittings were made in the upper part to connect the supply tubes for reagents and sample/carrier as well for the outflow to the detection flow cell. On its opposite (bottom) side, a confluence and a serpentine reaction coil of 0.8 × 0.8 mm were made using a 3-axis CNC controlled milling machine. The middle piece was then glued to cover the flow circuit applying a thin film of acrylic acid prior to tight fixation and a curing time of 1 h. In order to obtain a cavity below the flow circuit for the circulation of thermostat water, in the bottom piece as well as in the already glued assembly, two rectangular deepenings of 50 × 30 × 8 mm were milled prior to gluing both together. After curing, two flow connectors were attached to allow continuous flushing of the cavity with water provided by a peltier heating bath (PT31, Krüss Optronic, Hamburg, Germany, type PT-31) via silicon tubes (ca. 20 cm, 1 cm id). By this, the cavity served as a heating source to accelerate the reaction in the flow circuit. The temperature of the PT31 was set to its maximum of 40.0 °C.

2.3. Flow analyzer

The implemented MSFIA system for the determination of iodide is shown in Fig. 1. All liquid contacted parts were chemical resistant polymers, namely, ETFE, PMMA, and PTFE. PTFE tubing of 0.8 mm id was used for the flow lines of the manifold.

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