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Iodine speciation in coastal and inland bathing waters and seaweeds extracts using a sequential injection standard addition flow-batch method

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ABSTRACT

The present work describes the development of a sequential injection standard addition method for iodine speciation in bathing waters and seaweeds extracts without prior sample treatment. Iodine speciation was obtained by assessing the iodide and iodate content, the two inorganic forms of iodine in waters. For the determination of iodide, an iodide ion selective electrode (ISE) was used. The indirect determination of iodate was based on the spectrophotometric determination of nitrite (Griess reaction). For the iodate measurement, a mixing chamber was employed (flow batch approach) to explore the inherent efficient mixing, essential for the indirect determination of iodate. The application of the standard addition method enabled detection limits of 0.14 μM for iodide and 0.02 μM for iodate, together with the direct introduction of the target water samples, coastal and inland bathing waters. The results obtained were in agreement with those obtained by ICP-MS and a colorimetric reference procedure. Recovery tests also confirmed the accuracy of the developed method which was effectively applied to bathing waters and seaweed extracts.

1. Introduction

Iodine is one of the most abundant micronutrient in sea water and it is essential to all animals, including humans. In fact, the human diseases associated with iodine deficiency (IDD's) have been extensively reported by the World Health Organization [1,2]. However, the excessive intake may also result in a negative impact in human health, evidencing iodine importance as micronutrient [3,4].

Iodine may be found in water, air, soil, plants and animals but the most important source is seawater where it is mainly present as iodide (up to 50% in surface seawater) and iodate, with a minor fraction of dissolved organic iodine. So, the determination of the two inorganic forms enables to assess the iodine content and is very important to understand the geochemistry of the oceans [5,6]. Iodate is the most thermodynamically stable form of iodine in seawaters, yet due to phytoplankton and bacteria degradation, iodate is depleted from surface waters originating iodide [6]. Still, iodine levels in bathing waters are expected to be low: about 40 μg I (as I^-) L^{-1} in surface coastal water, 60 μg I L^{-1} in deep ocean water and 3 μg I L^{-1} in fresh and estuarine waters [7]. In the case of marine algae, micro and macro, iodine is mainly present as iodide since both iodate and organoiodine are in the form of monoiodotyrosine and diiodotyrosine [5,6].

Furthermore, in brown seaweed, most of iodine is inorganic, namely iodide, while in green seaweed, iodine is mostly bound to organic molecules [8].

The most common methods employed for iodine determination are capillary electrophoresis and chromatography [5]. However, these methods present a relatively high acquisition cost and, when complex matrices are involved, laborious sample pretreatments are required. In this scenario, it would be quite advantageous to develop alternative methods resorting to common laboratory equipment, namely involving potentiometry and molecular absorption spectrophotometry. Nevertheless, these methods generally do not permit to reach the required detection limits. One way to overcome this drawback, without involving complex wet chemical procedures such as separation methods, could be the application of the standard addition method (SAM). With this calibration method, based on the addition of different and known amounts of analyte to a constant amount of sample, the analyte concentration in the sample is determined by extrapolation [9]. In the end, the minimization of matrix interferences

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Table 1
Bathing waters samples characterization and sampling locations; Temp., temperature; *G*, conductivity; DO, dissolved oxygen.

Sample type	Sample ID	Multiparameter probe					Geographical coordinates	
		Temp. (°C)	pH	*G* (μs cm^{-1})	Salinity	DO, O_2 (mg L^{-1})	Longitude	Latitude
Inland bathing waters	Pi2	9.26	7.00	27	–	11.93	41.810169	−8.416739
	Pi10	16.03	6.26	36	–	8.33	41.810169	−8.416739
	Pi11	17.53	6.94	36	–	9.17	41.847478	−8.41915
	Pi12	18.03	6.88	41	–	9.16	41.597742	−8.458111
	Pi13	17.43	6.59	29	–	8.95	41.609328	−8.40830
Coastal bathing waters	P2	12.67	7.90	49441	32.28	11.05	41.156169	−8.681656
	P3	12.62	7.91	49940	32.74	11.74	41.160739	−8.686025
	P9	13.27	8.02	48067	32.34	14.33	41.695406	−8.849944
	P12	16.91	7.77	53295	35.21	8.04	41.014356	−8.644575
	P13	16.15	7.81	47182	30.81	8.43	41.202553	−9.116675
	P14	16.50	8.07	47338	30.85	8.36	41.161086	−9.103453

of complex sample matrices is accomplished. In a conventional batch mode, SAM is a very laborious and time consuming process, because it requires a calibration curve per sample. Therefore, the implementation of SAM in flow analysis could be an efficient combination. In fact, the advantages of performing the standard addition method using flow injection analysis have already been described [9,10].

In this context, the objective of the described work was to develop a sustainable method for iodine speciation in complex matrices such as bathing waters and seaweed extracts by combining sequential injection (SI) technique with SAM. The bi-parametric determination of iodide and iodate using the same SI manifold with no need for sample pre-treatment was aimed.

The choice of sequential injection approach, among other possible flow analysis modes, was due to its relative advantages, such as the possibility to perform multi-parametric determinations and the easiness to couple different devices, namely gas diffusion/dialysis units, mixing chambers and packed columns, around the selection valve [11].

The iodide determination was attained using a combined iodide ion selective electrode (ISE) due to its selectivity and simple incorporation in the flow system. Furthermore, the use of potentiometric detection is not influenced by the sample colour or turbidity. The SAM was implemented in-line by the sequential aspiration of the different standard solutions and sample.

Iodate was measured indirectly through the determination of nitrite in a sequence of two reactions [12]: (i) oxidation of hydroxylamine by iodate with production of nitrite and iodide; and (ii) Griess reaction for the determination of the formed nitrite: diazotisation of sulphanilamide by nitrite in acidic medium and the coupling of the intermediate with N-(1-naphthyl)-ethylenediamine hydrochloride (N1NED) to produce a coloured azo dye possible of being determined by spectrophotometry. To improve the oxidation of hydroxylamine by iodate, which is a relatively slow reaction, the mixture of the reagent and sample was enhanced by using a mixing chamber (MC), in a flow batch approach. A flow-batch system corresponds to the incorporation of a MC into the flow system, this way combining the advantages of batch and flow analysis, namely improved mixing between reagents and sample in a reproducible way [13]. By choosing this approach, not only a more efficient mixing is achieved, but the possibility of implementing stop periods to increase the reaction time was enabled. As the iodate concentration was calculated through the nitrite determination, based on the Griess reaction, the nitrite content of the samples was also assessed using a previously described method [14]. In the end, the nitrite content of the sample was subtracted from the assessed value that corresponded to the iodate plus nitrite in order to calculate the iodate concentration in the sample. As previously mentioned, to achieve the expected low levels of iodate and to minimize matrix interference, SAM was used and performed in-line. But in this case, fully exploring the flow-batch approach, SAM was accomplished using a single standard solution. With the MC placed in a side port of the selection valve, additions of different volumes of the standard solution combined with different volumes of deionized water (in line preparation of the standard solutions) were sent to the MC and added to the same sample volume for the in line standard addition procedure.

2. Experimental

2.1. Reagents and solutions

All solutions were prepared with analytical grade chemicals and boiled deionized water (specific conductance of less than 0.1 μS cm^{-1}).

Iodide stock solution of 100 mM was prepared by weighing 1.7 g of the previously dried KI (Merck, Darmstadt, Germany) in 100 mL of water. Standard solutions were prepared by dilution of the stock solution in the range 5.00–500 μM.

The ionic strength adjuster solution (ISA) was daily prepared by dissolving 5.1 g of potassium nitrate (Merck, Darmstadt, Germany) in water with addition of iodide to a final volume of 500 mL providing a final concentration of 0.1 μM I^- and 0.1 M KNO_3.

Iodate stock solution of 100 mM was prepared by weighing 2.15 g of the KIO_3 solid (Riedel-de Haën, Seelze, Germany) in 100 mL of water. The standard solution of 20 μM was prepared by dilution.

Hydroxylamine hydrochloride solution was prepared by dissolving 3 g of the reagent (Sigma-Aldrich, Germany) in 18 mL of 4 M hydrochloric acid (Merck, Darmstadt, Germany) and diluting to 200 mL with water. A concentration of 15 g L^{-1} hydroxylamine and 0.36 M HCl were obtained.

A stock solution of *ortho*-phosphoric acid (Merck, Darmstadt, Germany) 5 M was obtained from the concentrated acid (d=1.71, 85%). The colour reagent was prepared by dissolving 5 g of sulfanilamide (Merck, Darmstadt, Germany) in 25 mL of 5 M *ortho*-phosphoric acid and by mixing with 0.5 g of N-(1-naphthyl)-ethylenediamine dihydrochloride, N1NED, (Merck, Darmstadt, Germany) dissolved in water. After homogenizing the mixture the volume was completed to 250 mL and final concentrations of 20 g L^{-1} sulfanilamide and 2 g L^{-1} N1NED in 0.5 M of *ortho*-phosphoric acid were obtained under these conditions.

Artificial seawater was obtained by dissolving 41.5 g NaCl (Merck, Darmstadt, Germany) and 15 g $MgSO_4 \cdot 7H_2O$ (Merck, Darmstadt, Germany) in water to a final volume of 1.5 L, according to Liang et al. [15].