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A micro-flow-batch analyzer with solenoid micro-pumps for the photometric determination of iodate in table salt

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ABSTRACT

In this study, a micro-flow-batch analyzer (μFBA) with solenoid micro-pumps for the photometric determination of iodate in table salt is described. The method is based on the reaction of iodate with iodide to form molecular iodine followed by the reaction with *N*,*N*-diethyl-*p*-phenylenediamine (DPD). The analytical signal was measured at 520 nm using a green LED integrated into the μFBA built in the urethane–acrylate resin. The analytical curve for iodate was linear in the range of 0.01–10.0 mg L^{-1} with a correlation coefficient of 0.997. The limit of detection and relative standard deviation were estimated at 0.004 mg L^{-1} and < 1.5% (n=3), respectively. The accuracy was assessed through recovery test (97.6–103.5%) and independent analysis by a conventional titrimetric method. Comparing this technique with the conventional method, no statistically significant differences were observed when applying the paired t–test at a 95% confidence level. The proposed microsystem using solenoid micro-pumps presented satisfactory robustness and high sampling rate (170 h^{-1}), with a low reagents consumption and a low cost to build the device. The proposed microsystem is a new alternative for automatic determination of iodate in table salt, comparing satisfactory to the recently flow system.

1. Introduction

Iodine deficiency is a major public health problem for populations throughout the world, particularly for pregnant women and children [1]. It is estimated that more than two billion people have insufficient iodine intake [2]; thus most countries have resorted to iodine supplementation and monitoring programs. The most appropriate way to reduce this problem is by means of the universal salt iodization because of its widespread consumption as well as for economic considerations [3]. Iodine is normally added to salt in the form of potassium iodide (KI) or potassium iodate (KIO_3). In Brazil, the limits for salt iodination were set at 20–60 mg iodate/kg of salt [4].

The determination of iodate in table salt is usually performed by official AOAC method [5] which is based on the oxidation of iodide by iodate in acidified medium and subsequent titration of the generated iodine using a standard solution of sodium thiosulfate. Alternatively, several analytical techniques have been reported for the determination of iodate in salt and other matrices [6]. Such methods, when using automated flow analysis techniques [7–9], present advantages as, for example, reduction of the human effort, more precise analysis and an increase of the sample rate. Nevertheless, this type of system presents disadvantages, such as need of frequent recalibration and manual adjustment of the system, low sensitivity due to the sample dispersion and inefficient homogenization in the system, besides the necessity of carrier fluid which generates a high volume of residues [10].

These inconveniences have been overcome by using the flow-batch analysis (FBA) [11]. The FBA is an automated system that uses an instantaneous stop chamber and integrates batch and flow methods by using programmed multi-commutation [12]. The main component is the mixing chamber where the whole analytical process, including fluids addition, sample pretreatment, homogenization, precipitation, extraction, preparation of standard solutions, and detection, takes place under the total control of the software [10,13,14]. The sample is processed seamlessly with less: manipulation, consumption of reagents and samples, waste and chance for human error [15].

Recently, the flow-batch analyzer was miniaturized (μFBA) and applied for the determination of the Fe (II) in iron-based supplements (oral solutions) using the 1,10-phenanthroline method [16] and tannin determinations in green and black tea using the photometric (ferrous tartrate) and turbidimetric (copper (II) in acetate medium) methods [17,18]. Micro-flow-batch analyzer (μFBA) was also used for the determination of phosphorus in biodiesel, employing the molybdenum blue

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method [19]. The microfabrication used deep ultraviolet lithography and photopolymerizable urethane–acrylate photoresist. It contained an integrated photometer based light emitting diode (LED) and phototransistor for detection, and a nylon wire homogenizing system.

As the conventional flow-batch [12], the micro-flow-batch analyzer also combines favorable characteristics of both flow and batch analysis system. As in the flow system, the transportation of reagents, samples or other solutions into the micro-chamber (μCH) are carried out in a flow mode, and, as in the batch system, the sample processing is carried out into μCH ("micro-beaker"). In these systems, as described in the previous studies [16,17], the following steps are performed: addition of the fluids, mixture/homogenization/reaction to generate colorful product into μCH, and absorbance measurement. After these steps, the μCH is emptied through waste. Before processing a new sample, the cleaning step is carried out. Thus, μFBA does not use the carrier fluid. A cleaning solution is only used to clean the micro-chamber ("micro-beaker").

In the previous applications, μFBA used peristaltic pump and solenoid valves, respectively, for the propulsion and commutation of the fluid. [16–18]. However, these components can elevate the analyzer costs and may become its miniaturization unfeasible. These drawbacks can be circumvented by using solenoid micro-pumps [19].

In the present study, the characteristics of μFBA with solenoid micro-pumps [19] are explored to develop a novel microsystem for the photometric determination of iodate in table salt. As in the previous paper [17], the proposed μFBA was also built in the urethane–acrylate resin, with LED 520 nm and phototransistor integrated into the micro-chamber. The microsystem is a new alternative for the automatic determination of iodate in table salt, comparing satisfactory to the recently flow system [8,9].

2. Experimental

2.1. Reagents solutions

All the reagents were of analytical grade and freshly distilled and deionized water ($>18\ M\Omega\ cm^{-1}$) was used to prepare all solutions.

A 100.0 mg L^{-1} IO_3^- stock solution was prepared by dissolving 0.0168 g of KIO_3 in water and completing the volume to 100.0 mL with water. Standard solutions with concentration of 0.01–10.00 mg L^{-1} IO_3^- were prepared in a 10.0 mmol L^{-1} HCl medium to use in both conventional titrimetric and proposed automatic methods.

A 250 mg L^{-1} *N,N*-diethyl-*p*-phenylenediamine (DPD) solution was prepared by dissolving 0.0250 g of solid in water and completing the volume to 100.0 mL. A 10 mmol L^{-1} KI solution was prepared by dissolving appropriate amounts of salt in water.

A phosphate buffer solution pH 6.3 (0.17 mol L^{-1} Na_2HPO_4 and 0.34 mol L^{-1} KH_2PO_4) was prepared by dissolving 2.40 g of Na_2HPO_4 and 4.60 g of KH_2PO_4 in water. Afterwards, the volume was made up to 100.0 mL with water.

The commercial urethane–acrylate photoresist, used for the fabrication of the μFBA, was acquired at Carimbos Medeiros Ltda, Brazil (MacDermid, flex-light trademark M050).

2.2. Sample preparation

Samples from several manufacturers were purchased from local suppliers in Joao Pessoa, PB. Samples were dried at 120 °C for 6 h. Afterwards, 0.25 g of each sample was dissolved in 25.0 mL of a 10.0 mmol L^{-1} HCl solution and was treated according to the proposed μFBA method.

2.3. Instrumentation

To fabricate the micro-chamber (μCH) in urethane–acrylate resin, we used a commercial UV light source (Fotolight-MD2-A4, Carimbos Medeiros Ltda, Brazil), with two sets of mercury lamps (BLB-15 W-T8, SCT black light).

For layout design of the μCH, the CorelDraw® X5 program was used. The layout printing was on polyester transparency films for laser printing using an HP LaserJet P2014. After UV exposure, channels on the substrate were revealed by the removal of the non-exposed resin with an ultrasonic bath (model UltraCleaner 800, Unique, Brazil).

2.4. Fabrication process and assembly of μFBA

Fig. 1 shows a photo of the microsystem and its dimensions. The micro-chamber (μCH) was fabricated based on the methodology described in the literature [16,17]. The homemade μCH about 100 μL of total volume was built in urethane–acrylate photoresist. A 64 μL volume with an optical path of about 5 mm was used for each determination. This microsystem is mounted onto a suitable support in a black (darkroom) box (10.0 cm × 8.0 cm × 4.0 cm), to preserve the system from the effects of spurious environmental radiation while in operation.

The fluids are added to solenoid micro-pumps of 8 μL ($\mu P_1 - \mu P_4$) and 20 μL (μP_5) per pulse (Biochem Valve Inc., Boonton, NJ, USA). Teflon® tubes with 0.5 mm internal diameter were used for fluids transport. A 0.4 mm nylon wire was used within the micro-chamber to ensure an efficient homogenization. The nylon wire was coupled to a CD/DVD–ROM motor drive (model MDN3GT3CPAC, 2000 rpm, 5 V dc).

The detection system integrated into the μCH was composed of a green LED 520 nm as source of radiation, and a phototransistor for detection. These devices, both LED and phototransistor having 5 mm of diameter, were mounted firmly inside the μCH [16].

All tasks, such as data acquisition, solenoid micro-pumps, and drive motor activation, were done using a USB interface (USB6009, National Instruments®), which activated a lab made controller module. The software was developed in LabVIEW® 7.1 (National Instruments®).

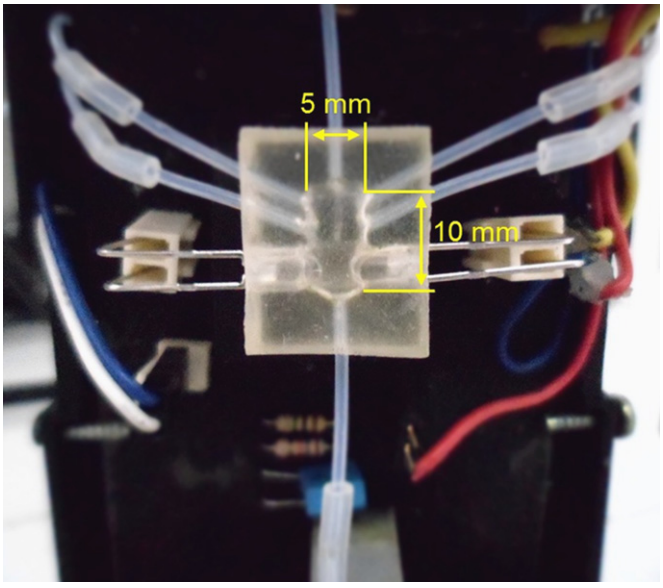

Fig. 1. Photograph of the microfabricated μFBA with its dimensions (mm).

2.5. Analytical procedure

The μFBA for the photometric determination of iodate in table salt is shown in Fig. 2. The analyzer was operated as described in Table 1. The solenoid micro-pumps were actuated at 5 Hz, yielding flow rates ranging from 1.2 to 9.0 mL min^{-1}.

The sample or standard solutions (2 pulses, μP_1) and 10.0 mmol L^{-1} KI solution (2 pulses, μP_2) were added simultaneously. The homogenization was performed by the drive motor (DM) coupled to the nylon wire (NW) for 2 s. In the sequence the DPD solution was added (2 pulses, μP_3) and the phosphate buffer solution pH 6.3 (2 pulses, μP_4) was homogenized again by DM for 2 s. After these steps, the absorbance is measured and the μCH is emptied (4 pulses, μP_5). The solutions are introduced or removed from the μCH, the inner air escapes by this air passage (in/out).

Afterwards, the μCH is cleaned by activation of μP_2 (8 pulses), adding the 10.0 mmol L^{-1} KI solution while activated, and the DM is activated for 2 s performing the agitation. Then, μP_5 is activated (4 pulses) to discard the contents of the μCH. This cleaning and discard procedure must be done twice to effectively clean the μCH.

The procedure for in-line blank preparation is similar to that described for the sample analysis. The difference is that 10.0 mmol L^{-1} HCl solution is used instead of the sample or standard solutions.

2.6. Reference method

For comparison, the proposed μFBA performance was evaluated by titration (AOAC official method) [5]. Standard solutions were prepared from 0.01 to 10.00 mg L^{-1} IO_3^- in a 0.01 mol L^{-1} HCl medium. In the titration, 10.0 mL aliquot of 12% (w/v) salt solution was transferred into an iodine stoppered flask. To the sample, 5.0 mL of 1.0 mol L^{-1} H_2SO_4 and 10.0 mL of 10% (w/v) KI were added. The mixture was titrated against a standardized $Na_2S_2O_3$ solution (about 2.4×10^{-4} mol L^{-1}), using 1% (w/v) starch as indicator [7]. The analysis of each sample was performed in triplicate and the concentrations were calculated from the analytical curve.

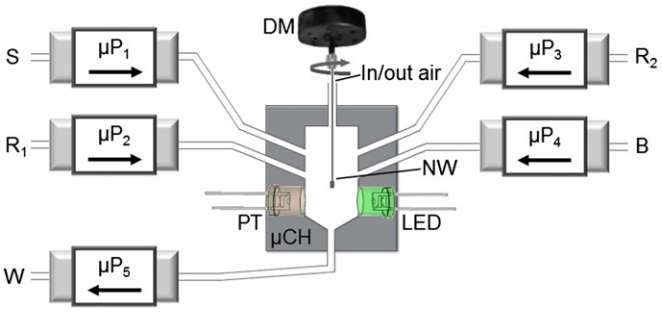

Fig. 2. The μFBA diagram. $\mu P_1 - \mu P_5$, solenoid micro-pumps; S, sample or standard solutions; R_1, 0.01 mol L^{-1} KI solution; R_2, DPD solution; B, buffer phosphate (pH 6.3); W, waste; μCH, micro-chamber (fabricated with urethane–acrylate resin [17]); DM, drive motor; NW, nylon wire; LED, light emitting diode; PT, phototransistor.

3. Results and discussion

3.1. μFBA parameters

The spectrophotometric method is based on the reaction of iodate with iodide to form molecular iodine [20] followed by reaction with DPD. Due to the excess of iodide, iodine is converted to I_3^- anion that reacts with the DPD, which is oxidized to a red-colored semiquinonoid cationic radical, DPD* (Wurster's dye) that presents absorption at 510 and 552 nm [8]. Considering this feature, a LED with maximum emission at 520 nm was selected as light source.

The proposed μFBA for the determination of iodate in table salt is similar to the analyzer described previously [19]. The analyzer uses LED and phototransistor inside the μCH facilitating the detection, as well as solenoid micro-pumps to improve the miniaturization and the portability of the method. The green LED with maximum emission at 520 nm was selected as light source. In μFBA, the μCH contains a nylon wire with a shovel tip that allows fluids agitation. The complete mixing of the solutions in the micro-chamber was obtained in less than 2 s, due to the high speed of drive motor (2000 rpm).

For the method employed, the concentration and volume of reagents, buffer and samples were evaluated in order to improve the sensitivity and reproducibility of the analytical signal. The system values selection (univariate method) was carried out in conformance with studied by Borges et al. [8]. All the optimization

Table 2
Selected parameters of the μFBA procedure for the determination of iodate in table salt.

Parameter	Evaluated range	Selected value
Hydrochloric acid solution (mmol L^{-1})	5–50	10
N,*N*-diethyl-*p*-phenylenediamine (DPD) solution (mg L^{-1})	100–500	250
Potassium iodide (mmol L^{-1})	1–100	10
Sample volume (μL)	8–32	16
Potassium iodide reagent volume (μL)	8–32	16
DPD reagent volume (μL)	8–32	16
Phosphate buffer solution (pH 6.3) volume (μL)	8–32	16
Total volume (μL)	32–80	64

Table 1
Switching course of the solenoid micro-pumps for the determination of iodate in the proposed μFBA[a].

Step	Description	μP_1	μP_2	μP_3	μP_4	μP_5	Pulses	Time (s)
1	Addition of the sample and reagent (S and R_1)[b]	1/0	1/0	0	0	0	2	0.8
2	Homogenization using the drive motor (DM)	0	0	0	0	0	0	2.0
3	Addition of the reagent and buffer (R_2 and B)[b]	0	0	1/0	1/0	0	2	0.8
4	Homogenization using the drive motor (DM)	0	0	0	0	0	0	2.0
5	Reading the analytical signal	0	0	0	0	0	0	1.0
6	Waste (W)	0	0	0	0	1/0	4	1.6
7	Cleaning with 0.01 mol L^{-1} KI solution (R_1)	0	0	0	1/0	0	8	3.2
8	Homogenization using the drive motor (DM) [c]	0	0	0	0	0	0	2.0
9	Waste of cleaning (W)	0	0	0	0	1/0	4	1.6

[a] Codes 1/0 and 0 indicate actuation of the solenoid micro-pumps and that the devices remain inactive, respectively.
[b] 2 pulses for each actuation of the micro-pump.
[c] The steps 7, 8 and 9 are repeated twice for every sample.

studies were performed automatically in the proposed μFBA. The range evaluated, and the values selected for each parameter are shown in Table 2.

3.2. Analytical characteristics

The proposed method obtained a satisfactory analytical curve for the determination of iodate in table salt with the regression equation $A=0.0124+0.7061C$; where A is the analytical response (in absorbance) and C is the concentration of the analyte in mg kg^{-1} of iodate in salt. The linear correlation coefficient, r^2, was 0.997 ($n=3$) in the range between 0.01 and 10.00 mg L^{-1}. Its analytical curve was statistically validated by the analysis of variance showing no lack of fit at a 95% confidence level.

The limit of detection (LOD) and the limit of quantification (LOQ) were 0.004 and 0.080 mg kg^{-1}, respectively. The LOD and LOQ for both methods were calculated based on the criteria established by IUPAC, the LOD was evaluated as three times the standard deviation of the blank measurement, and the LOQ was evaluated as being ten times the standard deviation of the blank measurement [21].

Table 3 presents the results obtained for the proposed μFBA for analysis, and those obtained for the conventional titrimetric method. No statistically significant differences at a confidence level of 95% were observed between the results when applying the paired t-test. We can also show satisfactory repeatability of the proposed method with a relative standard deviation (RSD %), less than 1.5% ($n=3$).

Recovery tests were also performed and, in this case, three samples were used. The volume of 1.0 mL standard solution with known iodate concentrations of 5.0, 10.0 and 15.0 mg kg^{-1} was added to 9.0 mL of the table salt (20.1, 31.8 and 7.9 mg kg^{-1} of iodate), for measurement using the proposed μFBA. The recovery values obtained are shown in Table 4. As can be seen, the recoveries obtained for each of the samples were within 97.6–103.5% range.

Table 3
Result for the determination of iodate in table salt using the proposed μFBA and the conventional titrimetric method (mg kg^{-1}). Mean values and uncertainties are based on three analytical determinations.

Samples	FBA		Reference	
	IO_3^- ± SD [a]	RSD %[b]	IO_3^- ± SD[a]	RSD %[b]
1	19.3 ± 0.3	1.5	20.1 ± 0.1	0.5
2	31.4 ± 0.2	0.6	31.8 ± 0.2	0.6
3	7.6 ± 0.1	1.3	7.9 ± 0.1	1.3
4	11.0 ± 0.1	0.9	10.6 ± 0.1	0.9
5	34.5 ± 0.3	0.9	34.1 ± 0.2	0.4
6	15.8 ± 0.2	1.3	16.2 ± 0.1	0.6
7	8.1 ± 0.1	1.2	8.4 ± 0.1	1.1
8	20.4 ± 0.1	0.5	19.8 ± 0.1	0.5
9	33.2 ± 0.2	0.6	33.5 ± 0.1	0.3
10	27.9 ± 0.3	1.1	27.4 ± 0.2	0.7

[a] SD, standard deviation of three replicates.
[b] RSD, relative standard deviation.

Table 4
Recoveries of iodate in table salt.

Samples	Recovery %		
	5.0 (mg kg^{-1})	10.0 (mg kg^{-1})	15.0 (mg kg^{-1})
1	100.7 ± 1.9	99.4 ± 2.3	102.1 ± 2.0
2	97.6 ± 2.1	101.9 ± 2.3	103.5 ± 1.6
3	102.8 ± 2.7	98.7 ± 2.2	103.3 ± 2.1

Table 5
Tolerance limits of foreign ions for the determination of 1 mg L^{-1} iodate in 5% (w/v) NaCl solution.

Ion	Added as	Tolerance limit (mg L^{-1})
F^-	NaF	10
Br^-	NaBr	250
K^+	KCl	1200
Ca^{2+}	$CaCl_2$ $2H_2O$	900
Mg^{2+}	$MgCl_2$ $2H_2O$	900

Table 6
Analytical characteristics of the proposed μFBA and other recent procedures from the determination of iodate in table salt.

Parameter	μFBA	MFA [8]	FIA [9]
Limit of detection (mg L^{-1})	0.004	0.017	0.02
Working range (mg L^{-1})	0.01–10.00	0.1–3.0	0.1–30
Relative standard deviation (%)	< 1.5 ($n=3$)	< 0.9 ($n=11$)	< 1.2 ($n=8$)
Sampling rate (h^{-1})	170	117	24
Sample consumption (μL)	16	54	200
Method	DPD[a]	DPD[a]	NED[b]
Integrated detection	Present	Absent	Absent
Carrier fluid	Absent	Present	Present

[a] *N*,*N*-diethyl-*p*-phenylenediamine.
[b] *N*-(1-naphthyl)ethylenediamine dihydrochloride.

The effect of some ions that might be present in table salt samples were studied, as was also done elsewhere [7]. This effect was investigated by spiking 5% (w/v) NaCl containing 1.0 mg L^{-1} iodate with known amounts of foreign ions and analyzing the solution by the proposed method under optimum conditions. An error of ± 3.3% was considered to be tolerable, as described in the literature [7,9]. The tolerance limit of the foreign ions is given in Table 5.

The analyzer presented an analytical frequency of about 170 samples per hour for the DPD method, with a waste generation of 192 μL per analysis.

Table 6 presents selected analytical features of the proposed μFBA, multicommuted flow analysis (MFA) [8] and flow injection analysis (FIA) [9], procedures for the determination of iodate in table salt. In general, the μFBA (compared to other procedures) presents satisfactory parameters, such as detection limit, working range, relative standard deviation (RSD %), sampling rate, elimination of the carrier fluid, and no associated fluid dispersion problems, such as loss of sensitivity.

4. Conclusion

The characteristics of the proposed μFBA with solenoid micropumps and integrated detection are explored for the determination of iodate in table salt. This method is advantageous when compared with other flow systems [8,9], because it is more sensitive and faster, it uses small quantities of samples and it does not utilize carrier fluid, generating less waste.

According to the experimental results, the proposed μFBA presents limits of detection and quantification, precision and accuracy compatible with the conventional titrimetric method and World Health Organization regulations [3] establish a maximum concentration of 40 mg kg^{-1} and 60 mg kg^{-1} in Brazil [5].

The proposed method is easy to be performed and offers results at a relatively low-cost, portability, robustness and more environmentally friendly. This way, μFBA may be a potentially

useful alternative for the iodate determination in routine analysis and being also suitable for the determination of other quality parameters in the same or in other matrices.

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