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Automatic determination of chlorine without standard solutions using a biamperometric flow-batch analysis system

Valberes B. Nascimento[a,*], Thiago M.G. Selva[a], Elaine C.S. Coelho[a], Francyana P. Santos[a], Jadielson L.S. Antônio[a], José R. Silva[a], Edvaldo N. Gaião[b], Mário C.U. Araújo[c]

[a] Universidade Federal Rural de Pernambuco, Departamento de Química, 52171-030, Recife, PE, Brazil
[b] Universidade Federal Rural de Pernambuco, Unidade Acadêmica de Serra Talhada, Caixa Postal 063, Serra Talhada, PE, Brazil
[c] Universidade Federal da Paraíba, CCEN, Departamento de Química, 58051-970, João Pessoa, PB, Brazil

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ABSTRACT

This study presents an automatic analysis system that does not require the use of standard solutions. The system uses an electrochemical flow cell for *in line* generation of the standards, and operates under the standard addition technique. The versatility of this system was demonstrated by the development of a one key touch fully automatic method for the determination of total available chlorine in real samples. The extremely simple, accurate and inexpensive method was based simply on the biamperometric monitoring of the well known redox reaction of chlorine with iodide ions in a flow-batch system, where the produced iodine (triiodide ions) generates an electrical current proportional to the chlorine concentration in the sample. The flow-batch parameters were optimized to maximize the sensitivity without losses on the precision of the analysis. An excellent linear dependence between the biamperometric signal and the chlorine concentration for the standard additions and a good agreement between the proposed approach and a reference method were obtained. The method was successfully applied to determine chlorine in several different bleach and chlorinated water samples ($r = 0.9995$, LOD = 8.261×10^{-7} mol L^{-1}) and could be easily extended to other oxidants and samples. Comparison to a reference method and recoveries close to 100% demonstrated the reliability of the proposed method. In addition, low residue disposal and reagent consumption, allied with high accuracy and precision, make it very promising for routine applications.

1. Introduction

Flow analysis systems have been extensively used on developing rapid, low cost, automatic and eco-friendly chemical analysis methods, especially to address clinical, industrial and environmental assays [1]. Innumerous approaches have made them useful on developing automatic chemical analysis systems that are able to carry on important analytical procedures such as standard additions and automatic flow dilutions [2–5].

Flow-batch systems, which combine useful uniqueness characteristics of the flow systems with well established classical batch mode approaches, have gained great attention in recent years, which can be demonstrated by some key examples [6–10]. A remarkable advantage of this association is how easy it is to carry out almost all the classical batch mode methods in a new and advantageous automatic instrumental approach. Briefly, a mixing/reaction chamber, containing a magnetic stirring bar, is inserted in a flow analysis system to allow all the chemicals to be thoroughly mixed, similarly to the classical batch analysis methods, before flowing to the detector for the monitoring of the analytical signal. Thus, efficient mixing and dilution of reagents, sample and any other solutions in a micro-liter range can easily be controlled through software.

While most flow analysis systems usually require a specific apparatus assembly for each particular method, strongly limiting their widespread acceptance at routine analysis laboratories, a flow-batch system can be viewed as a universal purpose accessory tool that can be easily attached to any conventional electrochemical or spectrochemical equipment. However, it seems that the main advantage of the flow-batch conception dwells on the fact that most classical methods can be updated to acquire a better precision and speed when performed in a flow-batch mode. This means maintaining the reliability of the classical batch mode methods while performing them with a modern, fully computer controlled and miniaturized mixing assembly accessory, that exchanges the use of large amounts of solutions by micro-volumes of samples and reagents, typically employed in flow analysis systems. Another important advantage is how easy it makes working with unstable

* Corresponding author. Tel.: +55 81 3320 6375; fax: +55 81 3320 6370.
E-mail address: valberes@dq.ufrpe.br (V.B. Nascimento).

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substances that are not well suited for the classical batch analysis. But, perhaps the most outstanding characteristic of the flow-batch approach is the possibility it offers for developing analytical methods through software.

There is an increasing importance on developing robust and simple analytical procedures for chlorine control in drinking waters, industrial effluents, industrial formulations and wastewaters [11]. Flow injection analysis has been largely employed on developing useful methods for the determination of chlorine in important samples. Most of the proposed methods are based on the spectrometric monitoring of redox reactions of chlorine with high sensitive chromogenic reagents, such as o-dianisidine [11], 3,3′-dimethylnaphthidine [12], tetramethylbenzidine [13] and o-tolidine [14]. A comparative study of the performance of chromogenic flow injection methods based on the use of o-dianisidine, 2,2-azino-bis-3-ethylbenzothiazoline-6-sulfonate (ABTS), 4-nitrophenylhydrazine, methyl orange, syringaldazine and indigo carmine, showed the ABTS as the most sensitive reagent [15]. Monitoring of hypochlorite by an environmental friendly native absorbance method [16], chemiluminescent test strip [17] and diffuse reflectance [18] have also been proposed. Highly sensitive electrochemical methods, based on the use of a selective electrode [19], square-wave voltammetry [20] and amperometric microfabricated sensor chips [21,22] have also been reported lately. Gas diffusion membrane-based approaches have led to highly selective methods [23,24]. Today, the literature reporting methods for the determination of chlorine is very extensive. Besides numerous attempts to develop novel, rapid, more selective and sensitive methods for the determination of chlorine, a substantial amount of research has been dedicated to the automation and improvement of existing methods [25]. Iodometric, amperometric and spectrometric methods with N,N-diethyl-p-phenylenediamine, syringaldazine and leuco crystal violet are considered as standard methods for the determination of chlorine in waters [26].

Sample treatment, preparation of standard solutions and system calibration are very time-consuming steps inherent to almost all analytical methodologies and may represent the limiting factor on the analysis speed in routine laboratories. The employment of unstable substances as standards is another important limitation. Some of these difficulties may be well addressed by the use of hyphenated techniques [27,28].

Biamperometric detectors have been applied for monitoring several important redox active substances [29–31]. Shortly, the current flowing between two polarized inert electrodes is a function of the concentration ratio of a reversible indicating redox couple [32,33], where a homogeneous redox reaction of the analyte with the reversible indicating redox couple produces the absent oxidized or reduced form needed to depolarize the system. Therefore, the change in the concentration ratio is the result of a quantitative redox reaction between the substance under analysis and a component of the redox couple.

The aim of this work was to develop an automatic system capable of carrying out analytical determinations by standard additions without the need of standard solutions. In the proposed system, which hyphenates coulometry with biamperometry, micro-amounts of a standard reagent are generated accurately *in line* by an attached electrochemical flow cell. Advantageously, since there is no change in the solution volume by the standard additions, the flow rates and the solution volume do not need to be precisely known. The system was successfully applied to carry on determinations of total available chlorine in commercial bleaches and chlorinated tap water samples without the need of the unstable chlorine standards, but it still could be applied to other samples and other analytes.

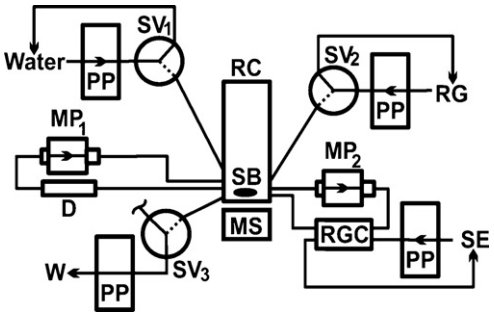

Fig. 1. Diagram of the flow-batch system: RC, reaction chamber; D, biamperometric detector; RGC, reagent generation cell; PP, peristaltic pump; MP, peristaltic micro-pump; SV, solenoid valve; MS, magnetic stirrer; SB, stirring bar; RG, reagent generating solution (KI 0.25 mol L^{-1}); SE, supporting electrolytic solution (Na_2SO_4 0.1 mol L^{-1}); W, waste. Arrows indicate sites and directions of pumping. For more details, see the text.

2. Experimental

2.1. Reagents and solutions

Chemicals were of reagent grade and used as received. The solutions were prepared with de-ionized water (Mili-Q® Plus 18 MΩ cm). A 0.25 mol L^{-1} potassium iodide solution and a 0.1 mol L^{-1} sodium sulfate solution were used as reagent generator and auxiliary electrolyte, respectively. Bleach samples with a chlorine tag concentration of 2.0–2.5% were acquired from local grocery stores and diluted (1:1000) before the analyses with de-ionized water. Chlorinated tap water samples collected from different sources were also analyzed.

2.2. Flow-batch assembly

Fig. 1 is a scheme of the flow-batch system. The main components are an eight channel-twelve rolls Gilson peristaltic pump, model Minipuls 3, employing Tygon® pumping tubes and polyethylene line tubes of 1.8 and 0.8 mm inner diameter, respectively; three three-way Cole Parmer solenoid valves, model 01367-72; two Bio-Chem peristaltic micro-pumps, model 090SP12; a 1.0 mL Teflon home-made reaction chamber, housing a 0.7 cm miniature magnetic stirring bar driven by a Hanna Instruments magnetic stirrer, model HI 190M; a Radelkis galvanostat, model OH 412, operating at a constant current of 487, 106.7 and 6.69 μA; a reagent generation cell [28] and a biamperometric flow cell [35]. A flow rate of *ca.* 1.0 mL min^{-1} was employed to deliver *ca.* 1.0 mL of the potassium iodide solution to the reaction chamber.

The whole assembly also includes a Personal Computer equipped with an ICP_DAS Analogical/Digital (AD) communication interface card, model A-8111; an electronic actuator module for TTL-level control of the solenoid valves and the micro-pumps and a user friendly home-made software for Windows® written in LabVIEW® 5.1 graphic language, for maneuvering the system, acquiring and handling data, and also for statistical calculations and the presentation of results.

The software was written in the graphic language LabVIEW® 5.1 and permits any unskilled operator to run the analysis without any hindrance. Actually, all the operator has to do is to press a start button and introduce the sample when required by the software. Then, all of the commands to control the whole system are synchronized to obey a previously defined procedure protocol that ranges from the number of reaction chamber washing cycles to the control of the length of time for the coulometric production of standards, data acquisition, statistical and concentration calculations, and results presentation on the screen, without any involvement of the operator.

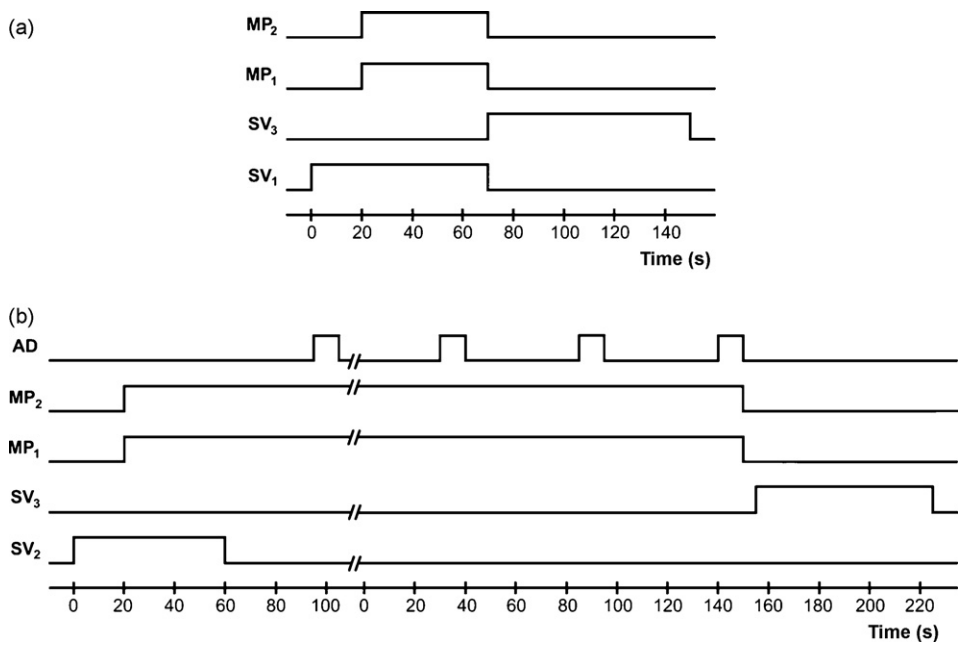

Fig. 2. Timeline diagrams of (a) the washing and (b) analysis protocols.

2.2.1. The reagent generation cell

The configuration and functioning of the reagent electrochemical generation cell was described elsewhere [28]. Briefly, it is a two-compartment coulometric flow cell that generates micro-amounts of reagents with high precision and accuracy. The generation solution flows in the anodic compartment while a reused auxiliary electrolyte flows in the cathodic auxiliary compartment. The cell operates under a 100% current efficiency.

2.2.2. The biamperometric detector

The configuration and functioning of the biamperometric detector was described elsewhere [35]. Briefly, it is a one-compartment flow cell containing two platinum wire electrodes polarized at *ca*. 100 mV. As in any conventional biamperometric detector, no current flows until the absent component of the employed electrochemical reversible redox couple is made present in the system. In this work, the reversible redox couple iodide/triiodide was employed. The iodide concentration is maintained at a high concentration while the triiodide is the absent component. This later can be produced by the reaction of the chlorine with iodide ($Cl_2 + I^- \rightleftarrows Cl^- + I_3^-$) or by the reagent generation cell ($I^- \rightleftarrows I_3^- + e^-$).

2.3. Procedure

The whole procedure is briefed by the ON/OFF timeline diagrams presented in Fig. 2. It should be said that the peristaltic pump (not in) is kept ON during the whole time and the ON/OFF micropumps controls are synchronized with that ones of the solenoid valves and the several data acquisition steps, made by the ICP_DAS Analogical/Digital communication interface card.

The system is fully automatic and controlled via software, the commands of which are briefed in the following lines.

2.3.1. System washing protocol

The system can be washed by pressing a wash button in the software control panel. On the starting threshold, while all the valves and micro-pumps are kept OFF, sodium sulfate, potassium iodide and water are continuously pumped back to their vessels. Then, the RC is filled up with water via SV_1. After a while, MP_1 and MP_2 are activated for a few seconds to wash the lines of D and RGC. Next, RC is emptied via SV_3.

2.3.2. Analysis protocol

Once the start button is pressed, the program asks for the number of washing cycles to be carried out (the default is three and the minimum is one). The final washing cycle always uses potassium iodide instead of water, by simply activating SV_2 instead of SV_1 in the washing protocol. After the wash step, *ca*. 1 mL of potassium iodide is introduced in the RC via SV_2. Then, MP_1 and MP_2 are turned ON to flow the solution through D and RGC during the whole analysis. At this instant, the system starts plotting the acquired current signals on the microcomputer screen to allow its visualization in real time (the results are saved also as an ASCII file); the signal from the blank is promptly acquired and the program asks to inform the volume of the sample that will be added by the operator (the default is 100 μL). After adding the sample, a restart button has to be pressed by the operator for the analysis procedure to be continued. Once the process is restarted, the signal from the sample is acquired and then three standard additions are automatically carried out, their signals being acquired consecutively. Finally, the RC is emptied via SV_3 and a washing cycle is carried out again.

The whole procedure takes around 6 min. Five current samplings (blank, sample and three standard additions) are recorded for each analysis, each one being the median of ten points measured during a 10 s sampling time period. Fig. 3 helps to understand the current sampling protocol.

For the analysis of bleach samples, volumes of 100 μL of diluted samples (1:1000) were employed and the standard additions were accomplished by applying a constant current of 487 μA during 10 s. However, for the analysis of chlorinated tap water samples the current magnitude was 106.7 μA and no dilution was necessary. Obviously, the magnitude of these parameters has to be chosen in accordance with the chlorine concentration range of the samples.

2.4. Reference procedure

Iodometric-based coulometric back titration was employed to validate the proposed method [26,34]. Briefly, an arbitrary amount of ascorbic acid is titrated in the absence and in the presence of a

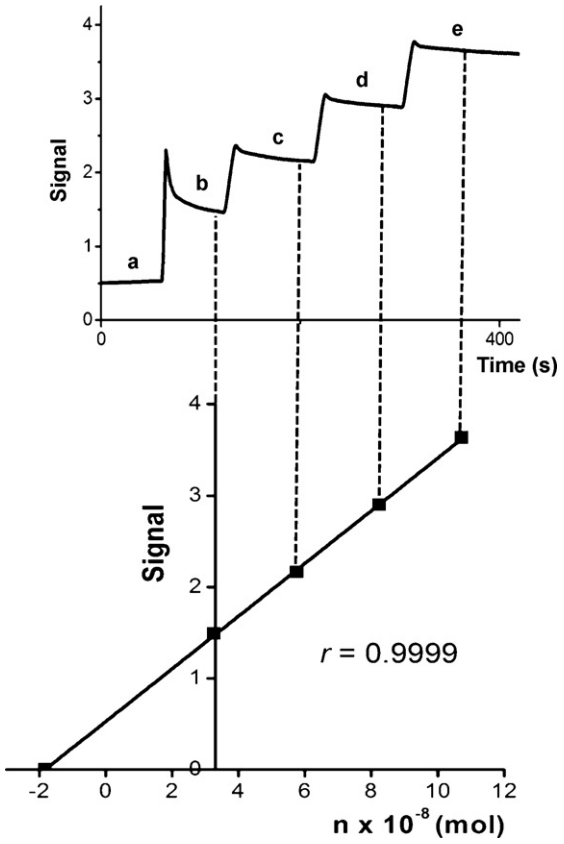

Fig. 3. Diagram of the current–time profile for a real analysis (a–e are the signals from the base line, sample and three consecutive standard additions, respectively, and the dashed lines points out the current sampling regions). '■' symbol represents the signal relative to number of mols.

fixed volume of the chlorine sample solution. The difference in the time spent for the titrations reveals the concentration of chlorine in the sample.

3. Results and discussions

3.1. Preliminary studies

The well known reaction in which iodide ions are oxidized to triiodide ions by chlorine can be carried out instantaneously and quantitatively in a neutral pH range. Thus, addition of chlorine or triiodide to the iodide solution contained in the RC cause the same effect at the analytical signal, since the former would promptly convert iodide to triiodide. Then, the coulometric production of triiodide by the electrochemical flow cell provides a way to carry on standard additions of "chlorine" by simply fixing the magnitude of the applied current and the generation time of the electrolysis. It should be noted that, as in any classical iodometric analysis, other oxidant species able to oxidize iodide to triiodide ions can interfere in the chlorine analysis.

The flow-batch parameters were studied. Since the RGC could be operated under 100% current efficiency regime in a range of current magnitudes up to *ca.* 2 mA [28], a number of combinations of generation times and current magnitudes could be employed to match several chlorine concentration ranges. The constant current and the generation time must be matched in accordance to the amount of standard to be delivered to the system. The upper limit of the constant current was established as that one in which the cell still operates under 100% of current efficiency, whereas the lower limit depends directly on the fixed generation time and on the sensibility of the detector. The employments of low generation times are important to reduce the total time of the analysis, but they are limited to the time response of the galvanostat. Thus, a generation time of 10 s was chosen to meet a compromise between precision and the time-span of the analysis, whereas current magnitudes of 487, 106.7, and 6.69 μA were chosen to match three different concentration ranges of interest. Lower current magnitudes were not tried, since at 6.69 μA the signal to noise relationship was small, but a further improvement in the electronic of the employed equipment could certainly lead to a lower operational concentration range.

The lengths of the flow lines that link the RC to its accessories (D, RGC and SVs) must be as short as possible to hasten the fluid deliveries and captures. Those lengths were typically of *ca.* 6 cm. Flow rates of *ca.* 1 mL min^{-1} were employed, although much higher values could be employed to shorten the whole analysis time.

As the calculations are based on the number of mols of triiodide, the volume of the solution delivered to the RC does not need to be known. In addition, the standard additions do not cause any volume change in the solution, since it encompasses only the electrochemical conversion of iodide to triiodide ions. Thus, it is not necessary to know precisely neither the volume of the solution inside the system, nor the flow rate of the flowing solutions, which is an important advantage of the method. The higher the flow rates inside the MPs, the faster the signal leveling off. Then a high flow rate of *ca.* 4 mL min^{-1} was fixed by a series of ON/OFF micropumps pulsation using a frequency of *ca.* 8 Hz. A sample volume of 100 μL matched well the bleach diluted (1:1000) samples and also the chlorinated undiluted tap water samples. A typical polarization potential of 100 mV, commonly used on biamperometric detectors was employed.

Fig. 3 shows a typical response for the analysis of a bleach sample by the proposed system using the above conditions, where an excellent linear response ($r = 0.9999$) is verified. A noticeable difference can be seen in the current profile caused by the sample addition, which is caused by the rapid introduction of the sample, differently from the relatively slow three consecutive standard additions. The leveling off verified after *ca.* 20 s shows the minimum elapsed time necessary to acquire a representative signal.

The whole procedure, and the calculations discussed bellow, is managed by the control software. The operator only has to start the software and introduce the sample.

The number of mols of chlorine added at each standard addition can be calculated using the Faraday's laws by the following equation, where i, t, and F are the magnitude of the applied current, time and the Faraday constant, respectively.

$$n_{Cl_2(added)} = \frac{it}{2F}$$

The number of molecules of chlorine present in the sample can be obtained from the intersection of the regression line with the "n" axis (Fig. 3). Thus, the concentration of chorine in the sample can be calculated taking in account the sample volume and the dilution factor.

As the generation cell operates under 100% constant current efficiency, the number of mols generated depends exclusively on the current magnitude and the generation time. Thus, the precision of the analysis will depend directly on the precision of the measurements of the sample volume and the triiodide generation times.

Despite its instability, the use of a triiodide solution as a standard offered no drawback at all for the analysis, since it was produced in a closed system and rapidly measured during the analysis.

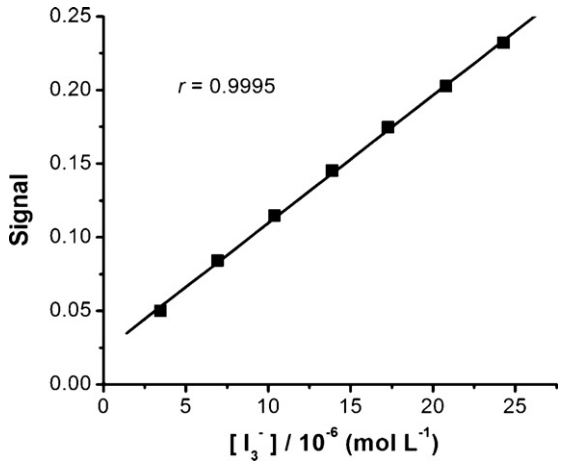

Fig. 4. Analytical curve. '■' symbol represents the signal relative to concentration of chlorine.

Table 1
Recovery study for chlorine determination ($n = 3$) in three different samples of chlorinated tap waters.

Sample	[Chlorine]/10^{-5} (mol L^{-1})			
	Found	Added	Recovered	Recovery (%)
1	1.501 ± 0.016	5.530	7.500	106.7
2	5.216 ± 0.060	5.530	10.82	100.7
3	0.926 ± 0.068	5.530	6.807	105.4

Table 2
Results of chlorine determination ($n = 3$) in five brands of commercial bleaches with a tag concentration of 2.0–2.5%.

Sample	Reference method (mol L^{-1})	Proposed method (mol L^{-1})	Relative error (%)
A	0.333 ± 0.001	0.331 ± 0.004	0.60
B	0.331 ± 0.001	0.333 ± 0.005	−0.91
C	0.333 ± 0.003	0.334 ± 0.007	−0.30
D	0.354 ± 0.002	0.345 ± 0.002	2.54
E	0.350 ± 0.001	0.352 ± 0.002	−0.57

3.2. Practical applications

Fig. 4 shows an analytical curve in the micromolar range ($r = 0.9995$, $(3.47–24.3) \times 10^{-6}$ mol L^{-1}, LOD = 8.261×10^{-7} mol L^{-1}) obtained with a current magnitude of 6.69 μA. The excellent performance of the system in that low concentration range permitted its application to the analysis of chlorinated tap water.

Table 1 summarizes the recovery study for three samples of chlorinated tap waters. Recoveries close to 100% demonstrated the reliability of the proposed method.

Five brands of commercial bleaches were analyzed. Table 2 summarizes a comparison study using the proposed method and the reference one. The results compared very well. The average relative error below 1% demonstrates the reliability of the proposed method.

4. Conclusions

A successful biamperometric procedure for a fully automatic determination of chlorine in commercial formulations and chlorinated water samples, based on standard additions of an *in line* electrochemical generated reagent, using the advantages of a flow-batch technique platform, was presented. It adjoins the favorable characteristics of both, the classical coulometric technique confidence and the flow-batch approach. Low consumption of reagents and waste generation make it a low cost and eco-friendly alternative to the already existing methods for routine analysis of chlorine. Besides the high sensitivity, the main advantage of the proposed approach is that it does not require standard solutions or special reagents. The method is well suitable for the determination of chlorine in bleaching products and chlorinated waters with a sample throughput of 10 samples per hour.

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