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An environmentally friendly flow-based procedure with photo-induced oxidation for the spectrophotometric determination of chloride in urine and waters

Diogo L. Rocha [a], Fábio R.P. Rocha [b,*]

[a] Instituto de Química, Universidade de São Paulo, P.O. Box 26.077, 05599-970 São Paulo, SP, Brazil
[b] Centro de Energia Nuclear na Agricultura, Universidade de São Paulo, P.O. Box 96, 13400-970 Piracicaba, SP, Brazil

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ABSTRACT

Chloride determination in urine and natural waters shows clinical and environmental importance because it can be related to human organism dysfunctions and water quality control. It is generally based on argentimetric volumetry or spectrophotometric methods with mercuric salts as reagents. Large amounts of highly toxic wastes then impair the greenness of procedures especially in batch mode. In this work, the use of hazardous chemicals was for the first time avoided in the spectrophotometric determination of chloride. The green procedure was based on a multi-pumping flow system, in which the analyte was on-line photoconverted to chlorine which was spectrophotometrically detected by methyl orange discoloration. The analytical response was linear from 2.0 to 20 mg L^{-1} chloride with a detection limit of 0.7 mg L^{-1} at the 99.7% confidence level. The coefficient of variation was 1.6% with a sampling rate of 75 determinations per hour. Usual concomitant species did not cause significant interference even in excess in relation to the highest concentration expected in the samples. The results for urine and water samples agreed with those obtained by the reference procedure at the 95% confidence level. The proposed procedure is then a fast, reliable and environmentally friendly alternative for chloride determination.

1. Introduction

Chloride is important for humans because it maintains electrochemical neutrality of extracellular fluids [1]. It is found in blood, urine, sweat and saliva and its quantification shows clinical importance, being related to the diagnosis of congestive heart failure, dehydration and syndrome such as Addison's disease [2]. Chloride determination in waters is also required for quality control because salinity can cause metallic plumbing corrosion and affect plants growth [3]. Therefore, regulatory agencies established a threshold limit of 250 mg L^{-1} for chloride in drinking [4] and natural waters [5].

The Standard Methods for the Examination of Waters and Wastewaters (SMW) [3] and the Association of Official Analytical Chemists (AOAC) [6] recommend procedures for chloride determination in natural waters based on argentimetric titrimetry or spectrophotometry with mercury(II) salts. The spectrophotometric procedure for chloride determination in urine also employs mercuric salts [1]. The best analytical alternative depends on the analyte concentration [7] but the overall disadvantage is the use of highly toxic and expensive reagents, which is an inconvenient mainly for routine work.

In view of the drawbacks of the reference procedures, some greener strategies have been proposed to minimize toxic waste generation, mostly employing spectrophotometry [8,9], potentiometry [10] or ion chromatography [11]. In spite of not requiring chemical derivatization and reach suitable detection limits for chloride determination in natural waters, ion chromatography [11] is time-consuming (10 min per sample), which impairs sample throughput. Potentiometry with ion-selective electrodes [1,10] is precise and widely employed in urinalysis, but it is largely susceptible to interferences [1]. Procedures which avoid toxic chemicals are the priority in green analytical chemistry [12,13], but this was not yet achieved in the spectrophotometric determination of chloride. For the development of greener alternatives, efforts have been made to minimize mercury consumption in the spectrophotometric chloride determination in urine and waters. Multisyringe [8,9] and multicommutation [14] approaches have been exploited to increase versatility and reduce mercury consumption compared to the SMW procedure [3] due to the intermittent reagent addition. This goal was also attained by using a solid-phase reactor based on mercury(II) thiocyanate immobilized on epoxy resin [15]. Moreover, long pathlength spectrophotometry [9] enhanced sensitivity and lowered Hg consumption. In spite of the minimization of waste amounts, mercury still was a source of environmental contamination.

In this work, a flow-based procedure with solenoid micro-pumps and on-line photochemical conversion was developed for greener spectrophotometric determination of chloride in urine and natural waters. The photoconversion of chloride yielded Cl_2 that caused the discoloration of the methyl orange dye.

* Corresponding author. Fax: +55 19 3429 4610.
E-mail address: frprocha@cena.usp.br (F.R.P. Rocha).

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2. Experimental

2.1. Apparatus

The flow system (Fig. 1) was designed with four solenoid micro-pumps (Biochem Valve Inc., Boonton, NJ, USA), which were operated at 5 Hz, a three-way solenoid valve (NResearch Inc., West Caldwell, NJ, USA) and polyethylene tubes (0.8 mm i.d.). The manifold was controlled by an Intel Pentium micro-computer through a parallel interface, employing a current drive based on the ULN2803 integrated circuit. Control software was developed in Visual Basic 6.0 (Microsoft).

Measurements were carried out with a multi-channel CCD spectrophotometer (Ocean Optics, Dunedin, FL, USA; model USB2000), with the software supplied by the manufacturer. Optical fibers transmitted the radiation from a tungsten-halogen lamp (Ocean Optics, model LS-1) to a 1.0-cm optical path flow cell (Helma) and from the cell to the spectrometer. The photo-reactor was constructed with a 13-W low-pressure mercury vapor lamp (Philips, TUV PL-S) which shows high emission at 254 nm. A 75-cm long thin-wall PTFE tube (0.8 mm i.d.) was coiled around the lamp bulb. The apparatus was inserted in a dark box without a cooling device.

2.2. Reagents and solutions

All solutions were prepared with deionized water and analytical grade chemicals. R_1 was a 75 mmol L^{-1} $K_2S_2O_8$ (Merck, Darmstadt, Germany) solution in 0.25 mol L^{-1} HNO_3 (Merck) and R_2 was a 75 μmol L^{-1} (25 mg L^{-1}) methyl orange solution in 0.3 mol L^{-1} HNO_3. Chloride 1000 mg L^{-1} stock solutions were prepared by dissolution in water of NaCl (Merck) previously dried at 110 °C for 2 h.

2.3. Proposed procedure

The flow manifold for chloride determination (Fig. 1) was operated according to the routine described in Table 1. Three sampling cycles (steps 1 and 2) were used for insertion of sample and oxidant (R_1) aliquots. The sample zone was carried to the middle of the photo-reactor PR (step 3) by the actuation of micro-pump P_3. The flow was stopped to increase sample residence time and thus the conversion efficiency (step 4). Afterwards, the digested sample zone was inserted into reactor B (step 5) in tandem (three sampling cycles) with aliquots of the R_2 reagent (step 6) and carried towards the flow cell (step 7). Measurements at 510 nm were based on peak height and carried out in triplicate. For sample replacement, micro-pump P_1 was operated while valve V was activated (step 8) to change the flow direction to waste. The sample aliquot between the confluence point x and valve V was then discarded by actuation of micro-pump P_3.

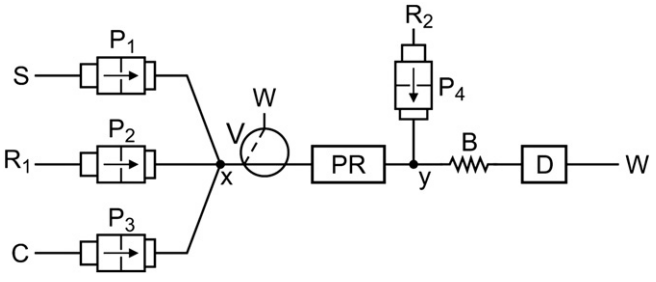

Fig. 1. Multi-pumping flow system for chloride determination. S: sample; R_1: 75 mmol L^{-1} $K_2S_2O_8$ in 0.25 mol L^{-1} HNO_3; R_2: 75 μmol L^{-1} methyl orange in 0.3 mol L^{-1} HNO_3; C: H_2O; W: waste vessel; P_1–P_4: solenoid micro-pumps; V: three-way solenoid valve; PR: photo-reactor (375 μL inner volume); x and y: confluence points; B: 100-cm long reaction coil; D: flow cell coupled to the spectrophotometric detector.

Table 1
Switching course of solenoid micro-pumps for chloride determination in natural waters.

Step	Description	Pump	Stroke volume (μL)	Pulses
1[a]	Sample insertion	P_1	10	6
2[a]	$K_2S_2O_8$ insertion	P_2	12	5
3	Sample zone transportation	P_3	20	2
4	Photoconversion (15 s)	–	–	–
5[a]	Digest transport	P_3	20	5
6[a]	Methyl orange insertion	P_4	20	1
7	Transport and detection	P_3	20	80
8[b]	Sample replacement	P_1	9	100
		P_3	20	50

[a] Three sampling cycles.
[b] Solenoid valve V switched on.

The analyte was photoconverted to Cl_2 which reacted with methyl orange yielding a colorless compound. The analytical signal was based on the difference between the reference (radiation absorption by methyl orange without reaction with chlorine) and sample signals. Chemical and volumetric parameters of the flow system were optimized by the univaried method. The effect of potentially interfering species usually found in urine (uric acid, urea, glucose, and creatinine) and natural waters (Fe^{2+}, Fe^{3+}, NO_2^-, Br^- and humic acid) was evaluated by addition to a 10 mg L^{-1} Cl^- solution.

2.4. Chloride determination in urine and natural waters

One tap and five natural water samples (from the Brazilian rivers Tocantins, Saltão, Piracicaba, Capivara, and Sorocaba) were filtered through 0.45 μm cellulose acetate membranes for the removal of the particulate material prior to analysis. Six urine samples were collected in 50-mL vials and analyzed after a 200-fold dilution without any additional sample treatment.

The reference procedure recommended by the Standard Methods for Examination of Waters and Wastewaters [3] and by clinical analysis reference [1] was employed to evaluate the accuracy of the proposed procedure. It was based on a flow injection system with continuous reagent addition. The sample was injected into a water carrier stream and mixed by confluence with the reagent composed by 600 mg L^{-1} $Hg(SCN)_2$ and 4.2 g L^{-1} Fe^{3+} in 0.15% ethanol and 50 mmol L^{-1} HNO_3. The formation of $HgCl_2$ and liberation of SCN^- ions yielded $[Fe(SCN)]^{2+}$, which was monitored by spectrophotometry at 480 nm.

3. Results and discussion

Spectrophotometric procedures for chloride determination are usually based on displacement reactions with mercury(II) salts [3,6]. On the other hand, several greener alternatives are available for chlorine determination, such as redox reactions which cause discoloration of dyes [16,17]. In the proposed procedure, chloride was photoconverted to chlorine employing $K_2S_2O_8$ and UV irradiation for generating oxidant radicals. Chlorine was then quantified by discoloration of methyl orange (MO), a dye with maximum absorption at 510 nm [17]. The flow system was constructed with solenoid micro-pumps [18] to improve mixing and minimize reagent consumption. The photo-reactor and reaction conditions were selected aiming higher sensitivity, best precision and minimization of the time for chloride photoconversion.

The mechanism involved on the methyl orange discoloration is controversial in the literature. Some authors cited that it is based on a redox reaction between chlorine and MO [7] while the chlorination and molecule breakdown was pointed out according to Eq. (1) [17]. A study around the reactions of azo-dyes in the presence of ClO^- and Cl_2 indicated MO chlorination as the probable mechanism [19]. This