FULL PAPER
THE ANALYST
www.rsc.org/analyst

o-Dianisidine: a new reagent for selective spectrophotometric, flow injection determination of chlorine

M. Catalá Icardo,[a] J. V. García Mateo[b] and J. Martínez Calatayud*[a]

[a] *Departamento de Química Analítica, Universidad de Valencia, Valencia, Spain. E-mail: jose.martinez@uv.es; Tel: /Fax: +34 96 386 40 62*
[b] *Departamento de Ciencias Químicas, Universidad Cardenal Herrera CEU, Moncada, Valencia, Spain*

Received 1st August 2001, Accepted 30th August 2001
First published as an Advance Article on the web 26th October 2001

A flow injection analysis (FIA) procedure for the determination of free chlorine in industrial formulations and water samples is proposed. The manifold is provided with a gas-diffusion unit which permits the removal of interfering species and also the preconcentration of chlorine. The determination of chlorine is performed on the basis of the oxidation by *o*-dianisidine as a chromogenic reagent to a coloured product which can be monitored at 445 nm. The method (for a preconcentration step of 60 s) is linear over the range 0.04–1.00 mg l^{-1} of chlorine, the limit of detection is 0.04 mg l^{-1}, the reproducibility of the procedure (as RSD of the slope) is 3.7% for a series of four independent calibrations, the precision (as RSD of a series of 30 continuous FIA peaks of 0.56 mg l^{-1} of chlorine) is 1.4% and the sample throughput is 40 h^{-1}. A detailed comparative study of the analytical characteristics of a single mono-channel reverse FIA assembly and the same system but provided with a Fluoropore membrane filter of 0.5 μm pore size was performed to check the advantages of the new approach in terms of sensitivity, selectivity and limit of detection.

Introduction

Chlorine is an important ingredient in different kinds of samples such as drinking waters, industrial effluents, swimming pools, industrial formulations and waste waters. It is toxic and its use has been linked to the production of other dangerous compounds such as the carcinogenic trihalomethanes; this has led to the increasing importance of robust and simple analytical procedures for chlorine control. Most of the existing papers devoted to chlorine determination are based on spectrophotometric methods involving different chromogenic reagents, such as *o*-toluidine,[1] *N*,*N*-diethyl-*p*-phenylenediamine,[2] 4-nitrophenylhydrazine,[3,4] methyl orange[1,5] and *o*-tolidine.[5] Widely employed methods for measuring chlorine residues are based on the use of *o*-tolidine. This method, although it appears to be sensitive, involves a carcinogenic compound and is subject to cation and/or chloramine (combined chlorine) interferences. In fact, the method developed by Palin,[6] in which residual chorine interacts with *N*,*N*-diethyl-*p*-phenylenediamine, producing a pink colour, has been claimed to be superior to the above method.

o-Dianisidine has been used in analytical chemistry in different ways. The oxidation reaction of *o*-dianisidine with H_2O_2 has been widely used in catalytic methods. Chromium,[7,8] phosphorus-containing pesticides[9] and phenols using various peroxidases[10] have been determined on the basis of their catalytic or inhibitory effects on the kinetics of this reaction. Dianisidine has also been employed as a mediator in electrochemical studies and procedures.[11] The photo-oxidation of *o*-dianisidine, which is sensitised by riboflavin,[12] has been used as a catalyst for the determination of Mn(II).[13]

Although a wide range of chemical reactions have been described with *o*-dianisidine as a chromogenic reagent, the analytical features of spectrophotometric methods for chlorine based on this reagent have been scarcely exploited. Momin and Narayanaswamy[14] proposed an optosensor for chlorine gas that consisted of dry reagent strips of nylon saturated with *o*-tolidine, *o*-dianisidine and *N*,*N*-diethyl-*p*-phenylenediamine solutions.

The implementation of gas-diffusion flow injection has been demonstrated to be an appropriate way to increase the selectivity in active chlorine determination.[15]

In this paper, a selective and sensitive method for the determination of free chlorine in industrial formulations and water samples is proposed. The reduction of interferences was achieved by porous-membrane permeation of chlorine. Residual chlorine was determined on the basis of the oxidation of *o*-dianisidine as a chromogenic reagent to a coloured product that can be monitored spectrophotometrically at 445 nm. An extensive study of the influence of interfering compounds on the chromogenic reaction was performed. The method compares favourably with other previously reported methods based on *o*-tolidine, *o*-toluidine or *N*,*N*-diethyl-*p*-phenylenediamine spectrophotometric reagents.

Experimental

Reagents

Chlorine standard solutions were freshly prepared from 10% w/v sodium hypochloride solution (Panreac) and were standardised iodimetrically.[16,17]

An appropriate amount of *o*-dianisidine (Fluka) was weighed and diluted with pure acetic acid (Probus) to obtain a solution 1 mmol l^{-1} in dianisidine such that when diluted with de-ionised water the final acetic acid concentration was 1 mol l^{-1}.

All solutions were prepared from analytical-reagent grade reagents and purified water (18 MΩ cm) obtained using reverse osmosis and then a Sybron/Barnstead Nanopure II water purification system provided with a fibre filter of 0.2 μm pore size. The following reagents were used: NaCl, $NaNO_3$, $Cr(NO_3)_3{\cdot}9H_2O$, $Na_3PO_4{\cdot}12H_2O$, $Ca(NO_3)_2{\cdot}4H_2O$,

$MnSO_4 \cdot 6H_2O$, NH_4Cl and EDTA-Na_2 from Probus, $Fe(NO_3)_3 \cdot 9H_2O$, $Na_2SO_4 \cdot 10H_2O$, $CH_3COONa \cdot 3H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, $Pb(NO_3)_2$, $Ni(NO_3)_2 \cdot 6H_2O$, KNO_3, NaF, $Cd(NO_3)_2 \cdot 4H_2O$ and $Cu(NO_3)_2 \cdot 3H_2O$ from Panreac, $Ba(NO_3)_2$ from UCB, $NaHCO_3$ from Guinama, KI and $ZnCl_2$ from Scharlau, $HgCl_2$, $AgNO_3$, $MnSO_4 \cdot H_2O$ and $Mg(NO_3)_2 \cdot 6H_2O$ from Prolabo, phenol from Doesder, sodium docecyl sulfate from Fluka and NaOH (AnalaR), sulfuric acid and hydrochloride acid from Merck.

To obtain a 100 mg l^{-1} chloramine solution, 0.535 g of ammonium chloride was dissolved in about 400 ml of water, adjusted to pH 7.5 with pH 8 borate buffer, slowly mixed with 100 ml of 1 g l^{-1} ClO^- (as NaClO) solution by gentle stirring and finally diluted to 1 l. The ammonium ion/hypochlorite mole ratio was 5 : 1. This solution was used as a mixture of monochloramine and dichloramine with an excess of dichloramine.

Chloramine-T (Scharlau) was used as a source of monochloramine. An appropriate amount of chloramine-T was diluted with nitric acid at pH 4.0.

Apparatus

The reverse flow manifold used comprised a PTFE coil of 0.8 mm id, two Rheodyne Model 5041 six-port rotary injection valves and a Gilson Minipuls 3 peristaltic pump.

The gas-diffusion unit was of the sandwich type and was made with two pieces of methacrylate screwed together; a groove carved in the pieces formed three parallel channels (8 cm long, 3 mm width and 0.2 mm deep), and the unit was split by the membrane, a Fluoropore membrane filter of 0.5 μm pore size (Millipore), which was held firmly between the two blocks.

Spectrophotometric measurements were performed with a Hewlett-Packard diode array spectrophotometer (Model 8452) provided with a flow cell of 18 μl inner volume from Hellma.

Flow injection analysis (FIA) assemblies

The proposed reverse FIA manifold is depicted in Fig. 1.

(a) FIA assembly. A reverse FIA assembly type was used, in which 48 μl of reagent were inserted into the sample stream [Fig. 1(a)].

(b) FIA assembly provided with a gas-diffusion device. Three different four-channel manifolds were tested [Fig. 1(b)]. They were provided with a gas-diffusion membrane to improve the selectivity and sensitivity of the method. Sample (channel Q_3) containing residual chlorine merged with HCl solution (channel Q_4); the total amount of chlorine in the sample was converted into chlorine and transported through the gas diffusion membrane. After an interval of stopped-flow (preconcentration time), the diffusion of chlorine to NaOH solution (Q_2, Q_5) acting as acceptor was performed. This basic solution caused the quantitative decomposition of chlorine into hypochlorite, which facilitated the gradient solution and transport process through the membrane. After the preconcentration step the resulting solution was forced to the flow system and merged with a solution of dianisidine (Q_1).

Procedures for preparation of samples

(a) Bleaches. Different kinds of commercially available bleaches were tested. Conejo, Estrella and Neutrex (all from Henkel Ibérica, Barcelona, Spain) and Alfonso (Salvador Alfonso Badía, Valencia, Spain) were selected in order to check the influence of different additives, namely anionic and non-anionic surfactants, perfumes and fibre protectors. No pretreatment other than dilution of the sample was needed.

(b) Tablets for sterilization. Five Milton tablets for sterilization (Procter & Gamble, Madrid, Spain) were powdered in an agate mortar and ground; an apropriate amount of the powder was weighed and diluted with de-ionised water to obtain a solution containing an equivalent amount of chlorine in the vicinity of 0.5 mg l^{-1}.

(c) Tablets of calcium hypochlorite. Barcolene CA-20 tablets used for treatment of drinking waters (Quimicamp, Utebo, Zaragoza, Spain) were treated as stated in the previous paragraph.

(d) Bottled mineral water. Two different commercial samples were spiked with chlorine standard solution: Bezoya from Ortigosa (Segovia, Spain), with chemical composition according to the label (mg l^{-1}) hydrogencarbonate 10.4, chloride 0.7, calcium 2.1, magnesium 0.3, sodium 2.5 and sílica 11.2; and Lanjaron, from Aguas de Lanjarón (Granada, Spain), with chemical composition according to manufacturer (mg l^{-1}) hydrogencarbonate 145.8, sulfate 25.9, calcium 38.1, magne-

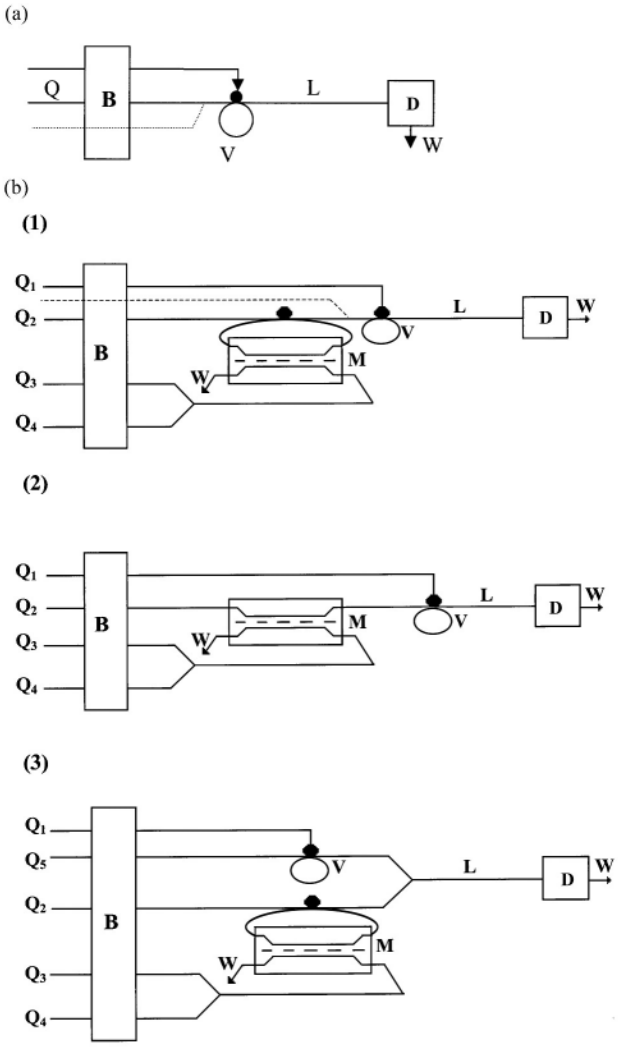

Fig. 1 Flow injection assemblies. (a) Reverse FIA system for preliminary studies. V, 48 μl; L, 60 cm × 0.8 mm id; Q, chlorine sample stream, 2.8 ml min^{-1}. (b) FIA assemblies with a gas-diffusion membrane. Q_1 dianisidine; Q_2 and Q_5, NaOH; Q_3, sample; Q_4, HCl; and M, microporous membrane. Dotted lines in (a) and (b)(1) represent the new added channel for interference studies.

sium 11.4 and sodium 6.8. Both of them were spiked with 5 ml of the chlorine standard solution (56 mg l^{-1}) and diluted to 500 ml with the sample; the final chlorine concentration was 0.56 mg l^{-1}.

The results obtained were compared with those provided by an official method.[17,18] based on the use of *N*,*N*-diethyl-*p*-phenylenediamine as titrimetric reagent and back-titration of the red compound formed by ammonium and iron(II) sulfate.

Results and discussion

Preliminary tests

The reaction in which dianisidine is oxidised by chlorine increases in complexity above pH 3, as suggested from cyclic voltammetric recordings.[11] For this reason, preliminary tests were conducted in an acidic medium (pH < 3), where the formation of the coloured species was simpler and more readily controlled.

Preliminary flow experiments were performed in a mono-channel FIA manifold in which a solution containing 3 mmol l^{-1} dianisidine in 2 mol l^{-1} acetic acid was used as carrier. This assembly, the simplest possible, where the sample was injected into the carrier-reagent stream, was changed and a reverse FIA assembly was adopted owing to the baseline drift through retention of some dianisidine on the walls of the PTFE tubing and the spectrophotometer flow cell. This new configuration diminished the blank signals and unwanted adsorption of the reagent owing to the flushing effect of the sample–carrier stream.

The influence of the nature of the reaction medium was studied by using 3 mmol l^{-1} dianisidine solution and constructing calibration graphs with the acids producing the most promising results. The acids tested included HOAc, HCl, H_2SO_4, HNO_3, H_3PO_4, H_2SO_4 and $HClO_4$. The best results were obtained in HCl and acetic acid media. In other media, either the chromogenic reagents not stable or the corrected absorbance (absorbance output minus the blank absorbance) was low. For identical analytical signals (corrected absorbance), HCl yielded higher blanks, and therefore acetic acid was found to be the optimum medium.

The spectrum of oxidised dianisidine was sensitive to changes in the acetic acid concentration. A two-channel continuous-flow assembly in which an acidic solution 3×10^{-3} mol l^{-1} in dianisidine merged with a 1.4 mg l^{-1} chlorine aqueous solution was used for checking the influence of acidic media on the spectra of dianisidine. From the spectra of the reaction product, two absorbance maxima at 378 and 694 nm appeared as relevant (Fig. 2).

Different calibration graphs for chlorine at 378, 445 and 694 nm were performed at two acetic acid concentrations, 0.15 and 2.0 mol ml^{-1}. The highest absorbances and slopes were obtained at 378 nm with 0.15 mol ml^{-1} acetic acid and at 445 nm with 2.0 mol l^{-1} acetic acid solution. Measurement of the absorbance of oxidised dianisidine at 445 nm with 2 mol l^{-1} acetic acid solution as carrier was adopted. This wavelength guaranteed better spectral selectivity in conjunction with a higher acetic acid concentration to facilitate the preparation of the reagent, which was obtained by direct dissolution of the solid in the amount of glacial acetic acid required.

The use of various temperatures (room temperature, 50 and 67 °C) and the presence of acetone or ethanol (20%) in the medium had no effect on the results.

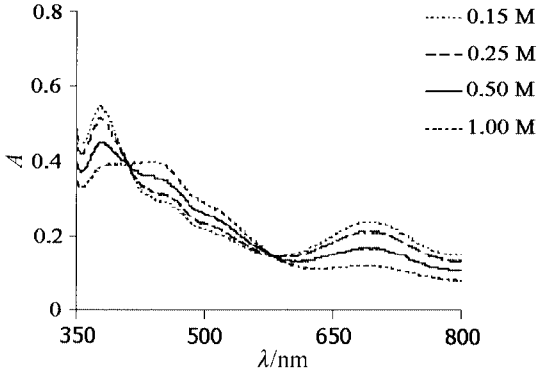

Fig. 2 Spectra of dianisidine oxidised at different acetic acid concentrations.

Optimisation of chemical and hydrodynamic parameters

The acetic acid and dianisidine concentration were optimised by examining their influence on the performance of the system over the ranges 0.15–2.0 and 4×10^{-4}–10^{-2} mol l^{-1}, respectively. Fig. 3 shows the variation of the signal with the concentration of dianisidine in a solution containing 0.63 mg l^{-1} of chlorine. The acetic acid and dianisidine concentrations chosen were 1 and 10^{-3} mol l^{-1}, respectively.

The FIA variables had no appreciable effect on the analytical signal owing to the fast kinetics of the reaction and the product was not immediately degraded under the working conditions used. The variables examined included the carrier flow rate, inserted reagent volume and reactor length. Table 1 shows the studied ranges and the values selected as optimum from the applied univariate methodology.

FIA assembly with a gas-diffusion membrane

To decrease the limit of detection and improve the tolerance of the system to potential interferents, the feasibility of preconcentration and separation of the chlorine was examined across a gas-permeable membrane. Three different FI manifolds were tested [see Fig. 1(b)]. A Fluoropore membrane filter of 0.5 μm pore size from Millipore was used in all assemblies. The membrane was sandwiched between two methacrylate blocks. The donor and acceptor solutions were circulated along the channels bounded by the carvings in the two blocks and the diffusion membrane. The general procedure in all assemblies

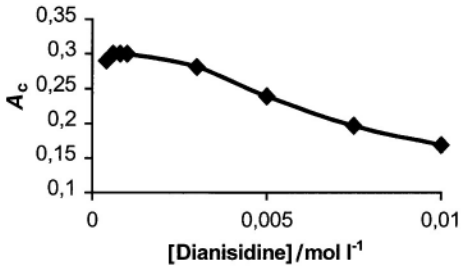

Fig. 3 Influence of the concentration of dianisidine. Concentration of acetic acid, 1 mol l^{-1}.

Table 1 Optimisation of FIA variables

Parameter	Without preconcentration: Range	Without preconcentration: Selected value	With preconcentration: selected value
Flow-rate/ml min^{-1}	2.7–6.8	6	Q_2: 5.6 Q_3: 4.6 Q_4: 0.6
Sample volume/μl	48–66	48	48
Reactor length/cm	28–80	80	68

was as follows: chlorine formed upon merging of the sample (Q_3) with an HCl stream (Q_4) was passed through the membrane and preconcentrated over a pre-set period during which circulation of the receptor stream (Q_2) was stopped. Once the flow had started, the solution of dianisidine (Q_1) was inserted into the system and the absorbance at 445 nm was measured.

The preconcentration/separation device was placed in the loop of a conventional injection valve. In manifolds (1) and (3) the flow was stopped during the preconcentration step by switching the valve to the loading position. In this way the receptor solution was not pumped to the detector. In manifold (2) the pump unit was stopped for a pre-set time.

Manifold (3) required only the control of the time of preconcentration. However, one additional channel is needed. As results of this configuration, the optimisation became more time consuming, the sample was diluted (the sensitivity and sample throughput decreased), more concentrated solutions of reagents were needed and the not easily reproducible simultaneous commutation of both injection valves was required.

Manifold (2) used an injection valve and only four channels were needed. However, two peristaltic pumps were required. The concentration time and the time from starting the flow until the insertion of dianisidine, essential for an optimal mixture of sample and reagent, must be controlled. The main disadvantage of this system was the poor control when the flow was stopped. The ideal system is a closed one, so that the receptor stream is not forced to flow owing to the pressure which tended to bend the membrane with use.

Considering the behaviour of the two manifolds (2) and (3), assembly (1) was selected as optimum. The sample containing chlorine (Q_3) flowing at 4.6 ml min^{-1} merged with HCl solution (Q_4) flowing at 0.6 ml min^{-1}. The analyte was converted into chlorine and transported through the gas diffusion membrane. The second valve in the loading position controlled the time of stopped-flow and then the time of preconcentration, which in turn means the volume of sample and diffusion of chlorine to NaOH solution (Q_2). This basic solution caused the quantitative decomposition of chlorine into hypochlorite, which facilitated the gradient solution and transport process through the membrane. After the preconcentration step and switching the injection valve, the volume in the loop where the membrane was placed is forced to the flow system and merges with a 1 mmol l^{-1} solution of dianisidine in 1 mol l^{-1} acetic acid (Q_1).

First the time between the insertion of preconcentrated chlorine and that of the dianisidine solution was studied over the range 1–6 s. The best results were obtained when the insertions were separated by 4 s.

The influence of the NaOH concentration in the acceptor solution (Fig. 4) and the concentration of the HCl solution were studied over the ranges 0–0.1 and 0.1–0.75 mol l^{-1}, respectively. The concentrations adopted were 0.005 and 0.5 mol^{-1} for a preconcentration time of 90 s and NaOH and HCl, respectively.

The reactor length was varied between 40 and 85 cm. The best compromise between reproducibility, peak height and sample throughput was obtained with a 68 cm long reactor.

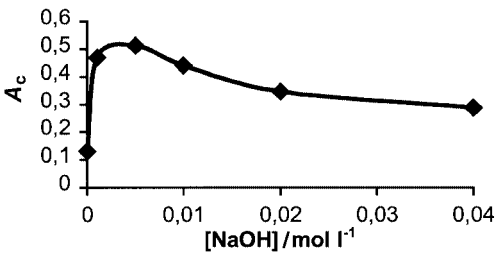

Fig. 4 Influence of the concentration of NaOH in the acceptor solution [see Fig. 1(b)].

The analytical performance of the system using the permeable membrane was tested at four preconcentration times, *viz.* 30, 60, 90 and 120 s. The results are given in Table 2. The long preconcentraton time resulted in higher sensitivity and lower limit of detection; however, it also decreased the linear range and throughput. Taking into account the level of chlorine in the samples and the advantages combined with higher sample throughputs, a 60 s preconcentration time was selected for further experiments.

Analytical applications

(1) Analytical characteristics. The linear range for chlorine was 0.04–1.00 mg l^{-1}, over which the analytical signal fitted a straight line with the equation $A = 0.82C - 0.040$ ($r = 0.998$), where A is absorbance and C is concentration in mg l^{-1}. The limit of detection (0.04 mg l^{-1}) was obtained as the concentration of chlorine which yielded an absorbance equal to the average blank peak plus 3 × RSD and was established by decreasing the concentration of injected chlorine until this relationship was reached. The repeatability of the system for a preconcentration time of 60 s was determined from 30 insertions of 0.56 mg l^{-1} chlorine solution (RSD = 1.4%). The RSD of the slope of different 4 d calibration graphs obtained in different working sessions was 3.7%. The sample throughput for 0.56 mg l^{-1} chlorine slution was 40 h^{-1}.

Table 3 compares these results with those obtained with the FIA manifold without a gas-diffusion membrane. As can be seen, the flow system provided with a membrane is more sensitive: with a preconcentration time of 120 s, the slope is four times greater. This reveals the increased efficiency of the diffusion unit, at the logical expense of linearity and throughput. The limits of detection are similar for both systems.

(2) Study of interferences. The dual function of the gas diffuser (*viz.*, preconcentration and interferent removal) led us to examine both systems in terms of selectivity. To this end, the influence of foreign species potentially accompanying chlorine in real samples on the analytical signal was studied.

Table 2 Influence of the preconcentration time

Preconcentration time/s	Equation[a]	Linear range/mg l^{-1}	r^2
30	$A = 0.4173C - 0.032$	0.14–2.00	0.9995
60	$A = 0.7378C - 0.0569$	0.11–1.10	0.9974
90	$A = 0.9997C - 0.0752$	0.08–0.86	0.9933
120	$A = 1.2916C - 0.0665$	0.08–0.67	0.9959

[a] A = absorbance; C = concentration (mg l^{-1}).

Table 3 Analytical characteristics of the FIA assemblies with and without preconcentration

Parameter	FIA assembly without preconcentration	FIA assembly with 60 s preconcentration
Equation[a]	$A = 0.311 + 0.13$ $r = 0.997$	$A = 0.820 - 0.040$ $r = 0.998$
Linear range/mg l^{-1}	0.35–2.30	0.04–1.00
Limit of detection/mg l^{-1}	0.04	0.04
Repeatability[b] (%)	1.1	1.4
Throughput (samples h^{-1})	80	40
Injected reagent (µl)	48	48

[a] A = absorbance; C = chlorine concentration (mg l^{-1}). [b] as RSD.

A merging point was required in both flow assemblies prior to the insertion valve for merging the interferent and chlorine solutions [see the dotted lines in Fig. 1(a) and 1(b)(1)]; in the latter the interferent solution was preconcentrated and the dotted line was used for the chlorine solution. A solution containing 0.63 mg l^{-1} chlorine was circulated through one channel and water (reference value) or the foreign species through the other; both streams were circulated at half their previous flow-rate. The concentration of foreign species was decreased to a level where the relative error in the determination was $<3\%$. The results are summarised in Table 4. The tolerance to the tested foreign compounds was clearly greater with the system provided with the microporous gas-diffusion device.

The selectivity of the oxidation of *o*-dianisidine and the efficiency of the gas-diffusion membrane as a physical and chemical barrier was also tested for Mn(IV) and chloramines, which can be produced in water samples as result of oxidation procedures. The influence on the oxidation of dianisidine was tested by using the manifold in Fig. 1(a) in which the solution of interfering compound was employed as carrier. The effectiveness of the membrane as a physical and chemical barrier was studied by checking the manifold depicted in Fig. 1(b)(1) for a preconcentration time of 60 s.

Although Mn(II) does not interfere in the proposed method for chlorine, it can, under slightly alkaline conditions, be oxidized to Mn(IV) by air. To reproduce the natural oxidation of Mn(II), air was bubbled for 2 h through a slightly alkaline solution at pH 9.5 containing 2 mmol l^{-1} Mn(II). The influence of the resulting manganese dioxide colloidal solution on the oxidative reaction of dianisidine was examined by diluting the previous solution 10-fold and injecting the chromogenic reagent into the resulting carrier solution. An absorbance of 0.18 was observed, indicating the fast kinetics of oxidation of dianisidine by Mn(IV). Using the manifold provided with a gas-diffusion unit, the response of colloidal manganese dioxide was similar to the RSD of the blank. The membrane thus acts as an efficient barrier against precipitates and even colloidal solutions and prevents the oxidation of the chromogenic reagent.

Table 4 Comparative study of interferences

	Without membrane		With separation by diffusion	
Interferent	Concentration/ mg l^{-1}	Error (%)	Concentration/ mg l^{-1}	Error (%)
AcO^-	200	−0.6	200	+1.8
Cl^-	500	−2.1	1000	+1.1
PO_4^{3-}	100	−2.5	200	−0.8
HCO_3^-	160	−2.4	240	−2.8
NO_3^-	1000	−2.7	1000	−1.6
I^-	0.5	+0.6	4	−3.4
F^-	25	+2.8	200	+0.22
SO_4^{2-}	300	−1.3	500	−0.4
NO_2^-	0.03	−3	0.2	−3.4
Na^+	325	−2.1	650	+1.1
K^+	200	−2.4	500	+1.3
Mg^{2+}	100	−3	100	−2.2
Zn^{2+}	100	−3	100	+2.6
Ca^{2+}	400	−0.7	500	−2.2
Cd^{2+}	25	−2.5	100	−1.8
NH_4^+	0.2	−2.9	100	−1.6
Ni^{2+}	10	−1.3	100	−2.5
Fe^{3+}	4	−1.7	100	+2.8
Mn^{2+}	10	−2.4	10	+3.2
Cr^{3+}	—	—	100	+0.24
Cu^{2+}	10	+0.7	100	+1.1
Ag^+	—	—	100	−2.3
Al^{3+}	25	−0.6	100	+1.1
Ba^{2+}	25	+0.3	100	−0.9
Hg^{2+}	—	—	100	+0.5
Pb^{2+}	4	+0.5	100	+0.6
Phenol	0.5	−1.8	5	+1.3
SDS	50	−3.2	200	+2.6

Monochloramine and dichloramine can be formed in presence of ammonium and nitrogen of organic amines according to the following reactions:

$$RNH_2 + HClO \rightarrow RNHCl + H_2O$$
$$RNHCl + HClO \rightarrow RNCl_2 + H_2O$$

Both chloramines were tested at two different concentrations, 1 and 5 mg l^{-1}. Using the manifold in Fig. 1(a) and for a concentration 1 mg l^{-1} of chloramine both compounds provided absorbances below the limit of detection of the method. For a concentration of 5 mg l^{-1} of chloramines an analytical signal equivalent to 0.209 mg l^{-1} of chlorine was observed. Using a preconcentration time of 60 s [manifold in Fig. 1(b)(1)], 1 mg l^{-1} of monochloramine and dichloramine gave absorbances corresponding to 0.076 and 0.080 mg l^{-1} of chlorine, respectively. For a concentration of 5 mg l^{-1} of chloramine, the responses observed (as mg l^{-1} of chlorine) were 0.250 for monochloramine and 0.293 for dichloramine. Taking into account the previous results, the linear equations obtained, the stoichiometry of the reaction involved in the production of chloramines, and assuming quantitative conversion of free chlorine into combined chlorine as chloramines, one can draw the following conclusions: (1) *o*-dianisidine is oxidised by mono- and dichloramine, but under flowing conditions no interference is observed at concentrations lower than 1 mg l^{-1} of chloramine; for 5 mg l^{-1} of chloramine the absorbance obtained was 6% in comparison with an equimolar solution of chlorine; (2) using a gas-diffusion membrane as interface and preconcentrating the sample, the analytical signals provided by chloramines were about 6% of those provided by solutions of chlorine containing the same molar concentration; (3) in this case, the membrane does not act as an effective barrier rejecting chloramines, but the chromogenic reaction with dianisidine is about 20-fold less sensitive for mono- and dichloramine than in the case of chlorine. This behaviour, probably due to a kinetic discrimination working under flowing conditions, would permit the selective determination of free chlorine in the presence of combined chlorine.

(3) Application to real samples. Finally, the two variants of the proposed method were applied to the determination of free chlorine in real samples, namely drinking water, bleach and sterilising tablets (Table 5). In all cases, the results were compared with those provided by a reference method based on the reaction of free chlorine with the indicator *N,N*-diethyl-*p*-

Table 5 Application to real samples. For details, see text. Results in mg l^{-1} unless stated otherwise. Top row, without preconcentration; bottom row, with 60 s preconcentration

Sample	Reference method[17]	Flow assembly	Error (%)
Bleach, Conejo	48570 ± 230	50100 ± 1600	3.2
	44290 ± 220	45400 ± 900	2.5
Bleach, Estrella	32700 ± 400	33800 ± 900	3.4
	28900 ± 400	29200 ± 1000	1.0
Bleach, Alfonso	43500 ± 400	44100 ± 1300	1.4
	39900 ± 400	41100 ± 500	3.0
Bleach, Neutrex	36600 ± 210	36700 ± 1300	0.3
	35000 ± 210	34700 ± 800	0.9
Barcolene CA-20[ab]	10960 ± 80	11000 ± 400	0.4
	10820 ± 80	10750 ± 60	0.6
Milton sterilization tablets[bc]	508 ± 12	515 ± 22	1.4
	505 ± 12	486 ± 4	3.8
Bezoya[d]	—	—	—
	0.531 ± 0.022	0.511 ± 0.011	−3.8
Lanjarón[d]	—	—	—
	0.510 ± 0.014	0.485 ± 0.011	−4.9

[a] Calcium hypochlorite tablets for treatment of drinking water. [b] Results in mg per tablet. [c] For cleaning baby feeding bottles. [d] Bottled mineral water. Not tested without preconcentration.

phenylenediamine (DPD) at pH 6.2–6.5.The chlorine was back-titrated with a ferrous salt.[18] Two different results were obtained for the analysed bleach and water treatment tablets (without or with preconcentration); the determination was performed without preconcentration and after a 6 week period with the preconcentration assembly. Both were compared on the same day with the reference method; the bottle (or the box of tablets) has been opened for 6 weeks a low chlorine content level was detected (like two different samples); however, the Milton tablets gave the same result as originally as consequence of each tablet being protected by a plastic cover.

Conclusions

An FIA–spectrophotometric procedure for chlorine determination is proposed. The method is based on the oxidation of *o*-dianisidine as chromogenic reagent. A comparative study of two FIA configurations (with and without a diffuser) was also performed. The best results were obtained with the assembly provided with the gas-diffusion membrane. The method exhibits excellent analytical features in terms of selectivity, sensitivity, limit of detection and linear range and compared favourably with regard to selectivity with other previously reported flow–spectrophotometric methods for chlorine determination.[1,3,4,19–21]

Acknowledgement

The authors acknowledge the European Commission–Directorate General XII for the financial support to this work in the proposal INCO Copernicus PL971118.

References

1 F. Cañete, A. Ríos, M. D. Luque de Castro and M. Valcárcel, *Analyst*, 1988, **113**, 739.
2 D. J. Legget, N. H. Chen and D. S. Mahadevappa, *Fresenius' Z. Anal. Chem.*, 1983, **315**, 47.
3 K. K. Verma, A. Jain and A. Townshend, *Anal. Chim. Acta*, 1992, **261**, 233.
4 A. Chaurasia and K. K. Verma, *Fresenius' J. Anal. Chem.*, 1995, **351**, 335.
5 D. J. Legget, N. H. Chen and D. S. Mahadevappa, *Analyst*, 1982, **107**, 433.
6 A. T. Palin, *J. Inst. Water Eng. Sci.*, 1986, **40**, 457.
7 C. Reis, J. C. de Andrade, R. E. Bruns and R. C. C. P. Morgan, *Anal. Chim. Acta*, 1998, **369**, 269.
8 B. M. Kneebone and H. Freiser, *Anal. Chem.*, 1975, **47**, 595.
9 A. L. Kapanadze, M. K. Beklemishev and I. F. Dolmanova, *J. Anal. Chem.*, 1999, **54**, 1047.
10 I. G. Gazaryan, D. B. Loginov, A. L. Lialulin and T. N. Shekhovtsova, *Anal. Lett.*, 1994, **27**, 2917.
11 Z. Shen, V. D. Parker and A. E. Aust, *Anal. Chem.*, 1995, **67**, 307.
12 T. Pérez-Ruiz, C. Martínez-Lozano, V. Tomás and O. Val, *Analyst*, 1994, **119**, 1199.
13 W. F. Beyer and I. Fridivich, *Anal. Biochem.*, 1988, **170**, 512.
14 S. A. Momin and R. Narayanaswamy, *Anal. Chim. Acta*, 1991, **244**, 71.
15 J. R. Gord, G. Gordon and G. E. Pacey, *Anal. Chem.*, 1988, **60**, 2.
16 J. Rodier, *Análisis de las Aguas*, Omega, Barcelona, 1981.
17 American Public Health Association, American Water Works Association and Water Pollution Control Federation, *Standard Methods for the Examination of Water and Wastewater*, American Public Health Association, Washington, DC, 14th edn., 1975, p. 354.
18 *Métodos Oficiales de Análisis*, Ministerio de Agricultura, Pesca y Alimentación, Secretaría General de Alimentación, Dirección General de Política Alimentaria, Tomo III, Madrid, 1994, p. 170.
19 Z. P. Wang, Y. J. Fang, L. Yuan and T. C. An, *Lab. Robot. Autom.*, 1999, **11**, 157.
20 Z. Zhang and Y. J. Zhao, *Analyst*, 1995, **120**, 1199.
21 J. Hernández Méndez, A. Alonso Mateos, M. J. Almendral Parra and C. García de María, *Quím. Anal.*, 1987, **6**, 60.