Solid-phase extraction and spectrophotometric determination of chlorine in air and residuals of free and combined chlorine in water utilizing azo dye formation

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Oxidation of phenylhydrazine-4-sulfonic acid to the 4-diazobenzenesulfonic acid cation and its electrophilic coupling with *N*-(1-naphthyl)ethylenediamine dihydrochloride to give an azo dye is a new reaction scheme that is proposed for the spectrophotometric determination (545 nm) of chlorine in air and free and combined chlorine residuals in environmental waters. Masking of free chlorine with acetone permitted the determination of combined chlorine residuals in water. The maximum molar absorptivity was found to be 1.46×10^6 l mol^{-1} cm^{-1}. A rectilinear calibration graph was obtained for 2.5–100 μg l^{-1} Cl. The azo dye could also be preconcentrated by solid-phase extraction on a C_{18} sorbent, leading to an enrichment factor of at least 40-fold. The limit of detection (without enrichment) was 0.2 μg l^{-1} Cl. Up to 50 μg l^{-1} bromate, 10 mg l^{-1} chlorate, 40 μg l^{-1} copper(II) and 100 μg l^{-1} iron(III) did not interfere. Chlorine dioxide was removed by bubbling the water sample with nitrogen. A comparison of the proposed method with the standard 4-*N*,*N*-diethylaminoaniline procedure was made and advantages of the present method are noted.

Chlorine is used on a large scale for the disinfection of water and waste water, as a bleach in laundering and in the pulp and textile industries. Chlorine is highly toxic and its use has been linked with the production of trihalomethanes, which are carcinogenic.[1] This has led to concern over the public health significance of the materials but the practice of chlorination has not been abandoned.[2,3] Depending upon pH and the presence of ammonia, chloramines are formed which remain in the water after the chlorine has dissipated. Chlorine dioxide is an attractive alternative to chlorine but the major disadvantage of its use is that little or no residual disinfectant remains. Since free chlorine (Cl_2, HOCl and OCl^-) and combined chlorine (NH_2Cl and $NHCl_2$) have different germicidal capabilities and health effects, it is important to differentiate these species in order to assess contact times adequately. There are a variety of methods for determining the chlorine content of water samples, only some of which can distinguish between chlorine species.[4]

The three recommended standard methods[4] are the 4-*N*,*N*-diethylaminoaniline (*N*,*N*-diethyl-*p*-phenylenediamine, DPD), leuco crystal violet (LCV), and syringaldazine (FACTS) spectrophotometric methods; all three claim to possess the ability to so differentiate. The stability of the coloured product formed by DPD is poor, however, with fading commencing immediately. That combined chlorine either does not react with DPD or that the reaction is slow enough to permit unequivocal determination of free chlorine has been shown to be a false assumption by separate and detailed studies.[5,6] Other methods were found to be unsuitable since the coloured products were extremely unstable.[6] Modifications have been suggested in the DPD method utilizing the flow injection principle;[7] many oxidizing agents, such as iron(III), still interfere. Fairly specific for free chlorine are methods based on the bleaching of the colour of Methyl Orange[8] and Acid Yellow 17.[6]

In this paper, a new method for the determination of chlorine in air and free and combined chlorine residuals in environmental waters is described, involving azo dye formation and spectrophotometry. The method yields the total of available chlorine; however, masking of chlorine with acetone, when chloroacetone is formed, leaves combined chlorine unaffected, which can be determined separately, and free chlorine is obtained by difference. Solid-phase extraction (SPE) was used for preconcentration of the azo dye in order to achieve higher sensitivity.

Experimental

Equipment

All spectrophotometric measurements were made with an ATI-Unicam (Cambridge, UK) UV2-100 UV/VIS spectrophotometer using 1 cm matched quartz cells.

Solid-phase extraction cartridges, 2.8 ml, packed with C_{18} sorbent (500 mg) (Alltech, Deerfield, IL, USA) were used. The air sampling train (Fig. 1) consisted of two midget impingers (Alltech) with glass joints and Wheaton connection, 25 and 20 ml, respectively, connected in series with PTFE tubing; a bubble flow meter (Hewlett-Packard, Palo Alto, CA, USA), and a portable vacuum/pressure pump (Millipore-India, Mumbai, India). An all-glass 0.45 μm membrane filter unit (Millipore,

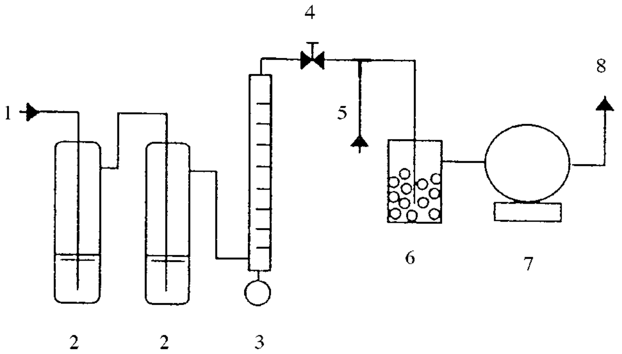

Fig. 1 Air sampling train. 1 = Air inlet; 2 = midget impingers containing PHSA reagent; 3 = bubble flow meter; 4 = needle valve; 5 = bypass; 6 = moisture trap; 7 = sampling pump; and 8 = pump exhaust.

Bedford, MA, USA) was employed for filtration of water samples.

Reagents

Phenylhydrazine-4-sulfonic acid (PHSA) as a 0.2% solution of analytical-reagent grade PHSA (Hopkin and Williams, Dagenham, Essex, UK) in 2 M hydrochloric acid and *N*-(1-naphthyl)ethylenediamine dihydrochloride (NED) as a 0.5% solution of NED (Eastman Kodak, Rochester, NY, USA) in 1 M hydrochloric acid were employed. 4-*N*,*N*-Diethylaminoaniline (*N*,*N*-diethyl-*p*-phenylenediamine, DPD) sulfate as a 0.5% aqueous solution was used. Both NED and DPD solutions should be kept protected from light and refrigerated when not in use.

Calibration standards and samples

A stock standard solution of hypochlorite was freshly prepared before use by dilution of a 5 ml portion of commercially available sodium hypochlorite solution, which contained 10–14% available chlorine, to 100 ml with water, and standardized iodimetrically.[4] A known volume of this solution was sequentially diluted to give 1 mg l^{-1} Cl solution. This solution was used within 1 h of its preparation.

To obtain a solution of 100 mg l^{-1} Cl present as monochloramine,[9] 0.535 g of ammonium chloride (BDH, Poole, Dorset, UK) was dissolved in about 400 ml of water, adjusted to pH 7.5 with pH 8 borate buffer, portionwise and slowly mixed with 50 ml of 1 g l^{-1} Cl solution and finally made up to 1 l. Less concentrated solutions were prepared by consecutive dilution of this solution, and used within 3 h of their preparation.

All water samples tested were freshly collected and filtered through a 0.45 μm membrane filter before analysis.

Preparation of calibration graph

Accurately measured 0.2–2 ml of calibration standards containing 5–100 μg l^{-1} Cl (free and combined) when diluted to 10 ml were treated with 2 ml of PHSA, shaken for about 1 min and then mixed with 0.5 ml of NED. The reaction mixture was again shaken for about 2 min, diluted to 10 ml with de-ionized water and the absorbance was measured at 545 nm in a 1 cm cell against a reagent blank.

Alternatively, 50–200 ml of sample solution were subjected to colour development as above, then treated with 0.5 g of sodium acetate and 25 g of potassium chloride (free from iodide and bromide), and passed through a C_{18} solid-phase extraction cartridge that had previously been activated and equilibrated by passing in sequence 2 ml each of methanol and de-ionized water. The retained azo dye was washed with 2 ml of de-ionized water and finally eluted with 2 ml of methanol. The eluate was mixed with 1 ml of 5 M hydrochloric acid, diluted to 5 ml with de-ionized water and the absorbance measured at 545 nm.

Analysis of unknown samples

A measured volume of sample solution was subjected to colour development as described under Preparation of calibration graph. The absorbance of the reaction mixture was referred to the calibration graph to determine the amount of total free and combined chlorine present.

Determination of combined chlorine

An aliquot of aqueous sample was mixed with 1 ml each of 1% acetone and 1% sodium carbonate and kept for about 20 min for masking of free chlorine. The solution was then subjected to colour development as above and the absorbance referred to the calibration graph.

Determination of chlorine in air

Each midget impinger of the air sampling train (Fig. 1) was charged with 5 ml of PHSA and 10–40 l of air were passed through at a flow rate of 350 ml min^{-1}. The trapping solutions were combined in a 25 ml calibrated flask and treated for colour development as described under Preparation of calibration graph.

Results and discussion

The chemistry

The inherent high sensitivity that is possible by a proper choice of reagents for azo dye formation used for the determination of nitrite by diazotization of an aromatic amine and coupling reaction with a phenol or another aromatic amine in sequence[10,11] suggested the use of an analogous reaction scheme for the determination of chlorine. The reactions proposed involve the oxidation of the hydrazino group of PHSA to yield the 4-diazobenzenesulfonic acid cation, which is subsequently coupled with NED to form an azo dye (Fig. 2). The key intermediate, the 4-diazobenzenesulfonic acid cation, is also obtained by diazotization of sulfanilic acid with nitrite. Therefore, the proposed reaction scheme was validated by comparison of the absorption spectra of the azo dye formed (i) on reaction of PHSA with free chlorine and coupling with NED and (ii) diazotization of sulfanilic acid and coupling with NED. The agreement was excellent.

Selection of reagents

All arylhydrazines should respond to the same colour chemistry as used with PHSA in the present method. In batch experiments, phenylhydrazine and four of its substituted derivatives were reacted with free chlorine in acidic medium and coupled with NED and the spectral properties of the azo dyes thus formed were determined (Table 1). Optimum absorbance was obtained with PHSA. The electrophilic coupling efficiency of the diazo cation formed on oxidation of an arylhydrazine may perhaps be the reason for the variation of the absorbance data in Table 1. NED forms a water soluble azo dye in the same acidic medium

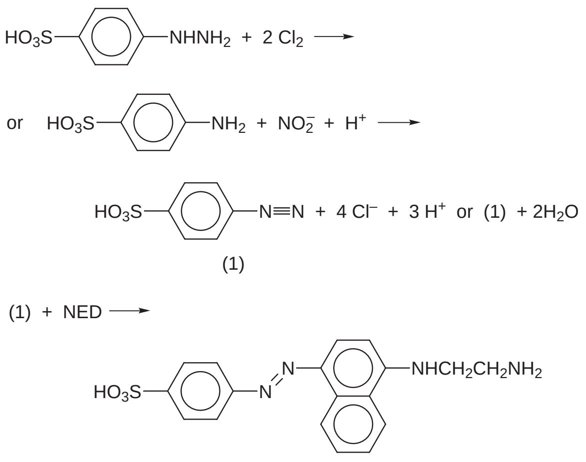

Fig. 2 Reaction of chlorine or nitrite with PHSA and coupling of the diazo compound with NED.

where the diazotization or oxidation reaction was carried out and was found to be the coupler of choice.

Optimization of conditions

Conditions were optimized for chlorine determination so that other oxidizing agents such as iron(III), bromate and chlorate do not interfere. The oxidation of the hydrazino group of PHSA occurs in acidic medium; a reagent solution in 2 M hydrochloric acid was optimum. With more concentrated acid there was positive interference from other oxidizing agents. The volume of PHSA and NED and the time for oxidation and coupling reactions were separately optimized by reacting 40 μg l^{-1} free chlorine under conditions where the parameter being evaluated was varied. For the entire concentration range of chlorine, 2 ml of 0.2% PHSA and 0.5 ml of 0.5% NED gave optimum absorbance.

For masking free chlorine without affecting combined chlorine, several reagents were tried. Glycine and sodium cyclamate (cyclohexanesulfamic acid), which have previously been used to suppress free chlorine interference,[12] after reaction with chlorine, still produce an azo dye in the PHSA method, ostensibly due to combined chlorine formation (*N*-chlorination). Hence, a masking reaction based on *C*-chlorination (where the product is not oxidizing) by substitution or addition was believed to serve the purpose. *a*-Chlorination of acetone proved to be the best method for masking the free chlorine; reaction with 1 ml of 1% acetone for about 20 min was optimum. Masking was carried out in the presence of sodium carbonate to avoid release of chlorine from combined chlorine.[6]

Solid phase extraction

Quantitative extraction of the dye on a C_{18} sorbent was achieved over the a pH range 4–7, which was maintained by addition of sodium acetate to the reaction mixture before extraction. As much as 200 ml of sample solution, after colour development, could be preconcentrated with about 98% recovery (RSD = 3%). SPE preconcentration was unaffected when acetone (1 ml of 1% solution in water) was used as a masking agent. The dye could be eluted with 2 ml of methanol. The azo dye produced in acidic medium is red–violet, however, the eluted dye after SPE is only yellow–orange. The original colour was restored after acidification with hydrochloric acid. There was at least a 40-fold enrichment.

Table 1 Comparison of spectral properties of azo dyes formed by phenylhydrazine and its substituted derivatives. Final free chlorine concentration, 40 μg l^{-1}

Reagent	$\lambda_{\max}$ of dye/nm	Absorbance
2,4-Dinitrophenylhydrazine	521	0.129
Phenylhydrazine	543	0.153
4-Nitrophenylhydrazine	544	0.658
4-Bromophenylhydrazine	559	0.925
Phenylhydrazine-4-sulfonic acid	545	1.192

Calibration graph and sensitivity

Free and combined chlorine residuals in water and chlorine in air produced the same linear regression in the present method. A rectilinear calibration graph was obtained over the range 5–100 μg l^{-1} Cl, the intercept, slope and correlation coefficient (*r*) being 0.0201 absorbance units, 0.0177 absorbance units l μg^{-1} and 0.9994 (n = 8; RSD = 1.2%), respectively. The limit of detection (S/N = 3) was found to be 0.2 μg l^{-1} for free and combined chlorine and 20 μg m^{-3} for chlorine in air (10 l of air sampled). After 40-fold analyte enrichment the detection limit was 0.01 μg l^{-1} Cl.

Application to spiked samples and comparison of results

Agreement, within ±2%, between the standard additions of chlorine to de-ionized water and the chlorine found by the present method served to validate the method. The results also agreed with those obtained by the standard DPD method;[4] a plot of PHSA data against DPD data was linear with a slope of 1.008, a *y*-intercept of 0.025 μg l^{-1} Cl and a correlation coefficient of 0.9996.

In experiments simulated for the determination of chlorine in air, known amounts of hypochlorite were added to 10 ml of de-ionized water in a midget impinger, which was connected to the sampling train (Fig. 1), acidified with 0.5 ml of 5 M hydrochloric acid and nitrogen passed through for 10 min at a flow rate of 350 ml min^{-1}. The pooled PHSA from two other impingers was subjected to colour development as described in the general procedure. The recovery of chlorine was 98.4% (RSD 3%); about 65% of chlorine was trapped in the first impinger.

Application to real samples

None of the samples tested mentioned in Table 2 was found to contain any chlorine residual, but they all showed chlorine demand. The present method was further validated by its application to natural waters after spiking with known amounts of free chlorine and determining the chlorine residuals. The PHSA method gives total chlorine residual but combined chlorine is obtained when free chlorine is masked with acetone; the free chlorine is found by difference. The results for total chlorine residuals obtained by the PHSA method agreed well with those of the DPD method. Results obtained for determining separate free and combined chlorine residuals are given in Table 2. The DPD method should also be applicable for chlorine

Table 2 Determination of free and combined chlorine residuals in natural waters

Sample[a]	COD[b]	Cl demand[c]	Residual free Cl[d]	RSD (%)	Residual combined Cl[d]	RSD (%)
Ground water	21	174	20.8	1.1	15.7	1.6
Surface water No. 1	386	1083	9.7	1.8	8.7	2.2
Surface water No. 2	73	1076	17.6	2.1	0.9	2.5
Tap water	0	74	16.4	0.8	22.2	1.8
Narmada River water No. 1	6	177	16.4	0.7	20.0	2.0
Narmada River water No. 2	7	219	11.9	0.9	23.7	1.9

[a] 20 ml of each sample were spiked with 40 μg l^{-1} of free chlorine. The chlorine residuals were determined after 10 min of spiking. [b] COD = chemical oxygen demand, mg l^{-1}. [c] Chlorine demand, μg l^{-1}. [d] Residual free and combined chlorine, μg l^{-1}. The results are averages of five determinations.

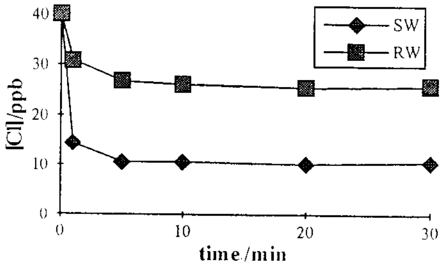

Fig. 3 Chlorine demand of environmental waters. SW = surface water No. 1 and RW = Narmada River water No. 2 in Table 2.

residuals speciation, by a batch procedure, if a secondary reaction of masking free chlorine with acetone is used in conjunction. The agreement of the results of Table 2 with the DPD results within ±2–3% (RSD 1–2.2%) served to confirm this view.

Known amounts of chlorine (hypochlorite) were added to two natural samples, one with a very high and the other with a very low COD value, and residual chlorine in the samples was determined. Despite the different levels of oxidizable materials present, both water samples showed optimum chlorine demand within 10 min (Fig. 3).

Interferences

In the study of the effect of matrix materials, interference was established when the result for chlorine residual was affected by more than ±2%. Large amounts of diverse ions did not interfere with the formation of the azo dye or its spectral properties. Nitrate, sulfate, phosphate, calcium(II) and magnesium(II) did not affect the results. Interference was believed to result from other oxidizing substances, as is the situation with many reagents, especially DPD. Nevertheless, up to 50 μg l^{-1} of bromate, 10 mg l^{-1} of chlorate, 30 μg l^{-1} of chlorite, 40 μg l^{-1} of copper(II) and 100 μg l^{-1} of iron(III) did not interfere. Chlorine dioxide was removed by bubbling nitrogen through the water sample adjusted to pH 7–8 without any loss of free or combined chlorine. Severe interference from hydrated manganese dioxide was noticed. Nitrite, although responding weakly to the colour test, can be decomposed by reaction with ammonium sulfamate.

Conclusions

Oxidation of PHSA in acidic medium by chlorine residuals to a diazonium cation and coupling of the latter with NED to yield an azo dye constitutes a simple, rapid and accurate method for the determination of chlorine. This method avoids many of the drawbacks of the DPD method such as the colour developed with chlorine being unstable, the absorbance should be measured immediately after the reaction and there is a false indication of high levels of chlorine residuals if other oxidizing agents, especially iron(III) and bromate, are present. The azo dye formed in the PHSA method is highly stable, and can be subjected to solid-phase extraction on a C_{18} sorbent, resulting in at least 40-fold enrichment and a limit of detection of 0.01 μg l^{-1} Cl. Without any enrichment the limit of detection was found to be 0.2 μg l^{-1} Cl. The proposed method has shown applicability in the speciation of free and combined chlorine residuals by using a pre-reaction with acetone to mask free chlorine. The PHSA reagent can be used as a trapping agent for chlorine in air utilizing the same chemistry.

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