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Organic Chloramine Analysis and Free Chlorine Quantification by Electrospray and Atmospheric Pressure Chemical Ionization Tandem Mass Spectrometry

Zoltan Takats, Kimberly J. Koch, and R. Graham Cooks*

Department of Chemistry, Purdue University, West Lafayette, Indiana 47907

Atmospheric pressure chemical ionization (APCI) and electrospray ionization (ESI), together with tandem mass spectrometry (MS^n), are used to study the mechanism of chlorination of amines and to develop a method for qualitative and quantitative determination of organic chloramines. Cyclohexylamine and 1,4-butanediamine (putrescine) are used as model compounds to investigate the mechanisms of the reactions between primary aliphatic amines and hypochlorous acid (aqueous Cl_2). The chlorination products are identified and characterized by collision-induced dissociation (CID) and H/D exchange. Chlorination occurs by electrophilic addition of Cl^+ and may be followed by HCl elimination, hydrolysis, or, in the case of diamines, amine elimination by intramolecular nucleophilic substitution. The relative rates of chlorination at amine and chloramine nitrogens are a function of pH and depend on the basicity of the amine. A novel method for active chlorine quantification using ESI or APCI mass spectrometry is suggested on the basis of the extent of chlorination of a sacrifical amine standard. This measurement has a limit of detection for *N*-chlorocyclohexylamine in the range of 0.1−10 μM, a linear dynamic range of 10^2-10^3, and an accuracy of ±10%, as determined for wastewater samples.

Chlorination of water is widely used for the disinfection of potable water. It is also used as a finishing step in wastewater treatment to inactivate bacteria used in prior biological treatment steps. Although many alternatives or supplements to chlorination have been developed, including ozonization and UV irradiation, chlorination remains the standard method of disinfection in many locations. The main advantage of chlorination is its ability to provide a stable disinfectant residual; a significant disadvantage is the formation of toxic disinfection byproducts with natural or xenobiotic organic compounds present in water.[1]

Aqueous chlorine reacts with organic compounds by a variety of routes, including electrophilic substitution and radical reactions. The disinfectant properties resulting from chlorination are attributed mainly to oxidation of nitrogen- and sulfur-containing species. These oxidation processes usually involve addition of Cl^+, derived from HOCl, to a nucleophilic site on the organic substrate. Addition is generally followed by nucleophilic displacement of the chlorine atom by an OH group (reacting as OH^-), or by hydrolysis or by homolytic dissociation of the N−Cl bond, forming N• radicals.[2−4] Nucleophilic substitution generally occurs by the S_N2 mechanism. The rates of S_N2 reactions at nitrogen centers are known to be considerably greater than those at carbon centers. Proton abstraction from the Cl^+ adduct by OH^- is an alternative reaction pathway.[5]

Insufficient chlorination of ammonaceous or ammoniacal water leads to the formation of a mixture of chloramines (monochloramine, dichloramine, and even nitrogen trichloride). These inorganic chloramines are also effective as disinfectant agents, so that in some cases the conditions of chlorination are intentionally set to promote formation of inorganic chloramines (a process known as "chloramination").[6]

At sufficiently high concentrations of active chlorine (hypochlorite, hypochlorous acid, and chlorine), a phenomenon known as breakpoint chlorination occurs. In breakpoint chlorination, ammonaceous and ammoniacal materials are completely oxidized to dinitrogen, and the active chlorine is simultaneously reduced to chloride. Thus, the amount of chlorine sufficient to reach breakpoint is determined by the amine content of the water to be chlorinated. It is important to chlorinate until breakpoint, because underchlorinated water may contain viable microorganisms. To detect breakpoint, it is necessary to have information on the active chlorine content of the water. This is achieved using methods discussed below.

The hydrolysis of inorganic chloramines produces hydroxylamine and, by subsequent oxidation, nitrous and nitric acid. However, these processes are comparatively slow, allowing inorganic chloramines to survive in water for days after treatment. Organic chloramines originate from the reaction of chlorine with

* E-mail: cooks@purdue.edu.

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organic amines or by chlorine transfer from inorganic chloramines to organic amines. These products can undergo further hydrolysis or oxidation; however, they are generally more stable than inorganic chloramines.[7,8] Chlorination of organic compounds can produce many other byproducts, such as cyanogen chloride, chloroform, chloroformamide, chloroacetonitrile, chlorinated amino acids, and chlorinated nucleic bases.[9,10]

Methods generally used for detection and quantitative determination of active chlorine and chlorination byproducts are *N*,*N*-diethyl-*p*-phenylenediamine/ferrous ammonium sulfate (DPD/FAS) titrimetry, colorimetry, gas chromatography−mass spectrometry (GC/MS), membrane introduction mass spectrometry (MIMS), or spectrophotometry.[11−14] The main disadvantages of these methods are the restricted applicability (each is optimum for only one or two groups of analytes) and the complicated sample preparation required for all techniques (with the exception of MIMS, which is suitable for on-line determination but has so far been limited to the analysis of nonpolar, volatile compounds).[15]

Atmospheric pressure chemical ionization (APCI) and electrospray ionization (ESI) are being used in an increasingly wide range of applications. An advantage of these techniques is that they can easily be miniaturized, which should allow a compact system to be built to monitor the concentration of active chlorine and various chlorination byproducts after water treatment. As a step toward the development of a miniaturized system for water monitoring during disinfection, quantitative and qualitative analysis of chloramines was investigated by ESI and APCI mass spectrometry. The absence of literature on the general behavior of organic chloramines in ESI or APCI mass spectrometry further motivates this study. We have simultaneously begun a systematic study to investigate the reactions of free chlorine with amino acids using APCI and ESI mass spectrometry and found intermediates not observed using conventional GC/MS methods. The characterization of some chlorinated amino acid derivatives by electrospray has recently been described by Nightingale et al.[16]

EXPERIMENTAL SECTION

Reagents. Two alternative methods were used for chlorination. In one procedure, chlorinated water was prepared by saturating deionized water (10 mL) with chlorine gas. Chlorine was produced by the oxidation of hydrochloric acid (5 mL, concd, Mallinckrodt) using potassium permanganate (3 g, MCB Reagents). Excess chlorine was destroyed using a 5 M solution of $NaHSO_3$ ($NaHSO_3$, Fisher Scientific). All solutions containing free chlorine were treated with excess $NaHSO_3$ at the end of experiments. In the alternative method, 10 mM NaOCl solution was prepared by diluting a 4% stock solution (Sigma). All active chlorine-containing solutions were stored in the dark at low temperature (<4 °C) to avoid photochemical oxidation of Cl_2 to ClO_2. Dilute active chlorine-containing solutions were stored for no longer than 10 h for the same reason. Although both solutions were used in these experiments, it is important to note that only the NaOCl solutions were used for quantitation. The NaOCl solutions were chosen for two main reasons: (i) NaOCl generates free chlorine concentrations which are more stable (weeks), as compared with chlorous water, which decays nonlinearly at room temperature in a matter of hours; and (ii) standardized solutions of NaOCl are commercially available, whereas chlorous water must be made, and the concentration of free chlorine must be measured prior to each use.

Table 1. Experimental Conditions Used for APCI and ESI

parameter	APCI	ESI
infusion flow rate, μL min^{-1}	10−100	1−5
vaporizer temp,°C	120	
sheath gas flow, L min^{-1}	1	0.5
auxiliary gas flow, L min^{-1}	0.2	0.1
tube lens offset, V	−20	−20
discharge current/spray voltage	6 μA	3.5 kV
capillary temp, °C	120	120
capillary voltage, V	−22	−22

Cyclohexylamine hydrochloride (cyclohexylamine, Aldrich) solution (1mM) and 1 mM putrescine hydrochloride (putrescine, MCB Reagents) solution was prepared by dissolving the appropriate amine in deionized water. Ammonium chloride (Mallinckrodt) solutions were prepared by simple dissolution of the solid in deionized water.

Organic chloramine solutions were prepared by adding the chlorinating agent to the organic amine hydrochloride solution stepwise, with continuous mass spectrometric detection. Inorganic monochloramine solutions were prepared by the method of Shang and Blatchley.[15] As necessary, pH values of the solutions were adjusted by adding 0.1M HCl dropwise. Note that the compounds of interest were detected as protonated ions in the mass spectrometry experiments.

Procedures. H/D exchange experiments were carried out using D_2O as solvent instead of deionized water. Active chlorine determination was accomplished by diluting 1.00 mL of 0.5 M cyclohexylamine hydrochloride stock solution to 1000 mL with the appropriate water sample, followed by determination of *N*-chlorocyclohexylamine content by ESI- or APCI-MS. Solutions used to establish calibration curves were prepared by serial dilution from freshly prepared standard solutions. *N*,*N*-Diethyl-*p*-phenylenediamine/ferrous ammonium sulfate (DPD/FAS) titration of active chlorine concentration was carried out as described.[4]

Instrumentation. An LCQ ion trap mass spectrometer (Thermo Finnigan, San Jose, CA) equipped with both APCI and ESI sources was used. Source conditions are summarized in Table 1. A typical scan range was *m*/*z* 50−500 (Thomson). Tandem mass spectra were recorded using collision energies that were optimized

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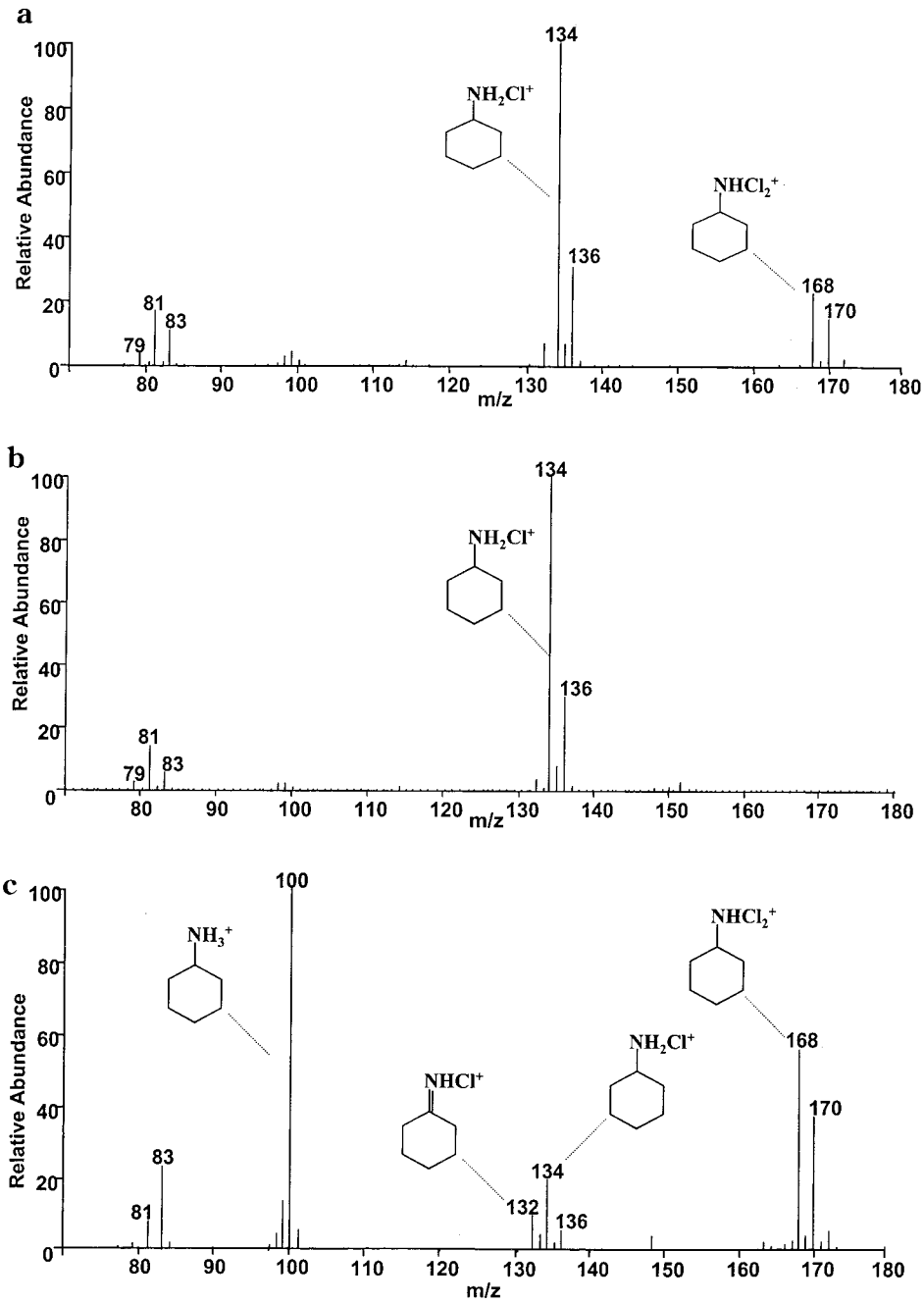

Figure 1. (a) Positive ion APCI mass spectrum of *N*-chlorocyclohexylamine generated at pH 6 from 1 mM cyclohexylamine (CHA) using 1 mM NaOCl. (b) Positive ion ESI spectrum of *N*-chlorocyclohexylamine generated at pH 6 from 1 mM CHA using 1 mM NaOCl. (c) Positive ion APCI spectrum of chlorinated cyclohexylamine generated at pH 2 from 1 mM CHA using 1 mM NaOCl.

for each experiment (typically 5−10%). These energies are expressed in terms of the manufacturer's nominal relative collision energy (%), for which the range from 0 to 100% corresponds to a resonance excitation AC signal of 5 V (peak-to-peak).

RESULTS AND DISCUSSION

APCI and ESI Characterization of Chloramines. *Aliphatic Monoamines (Cyclohexylamine).* Cyclohexylamine was selected as representative of a simple monofunctional amine. The positive ion APCI and ESI spectra of under-chlorinated cyclohexylamine (amine:Cl molar ratio > 1) are shown in Figure 1a,b. The monochloramine generated from the reaction mixture is readily ionized and produces a characteristic molecular ion using either ionization method. The APCI spectrum (Figure 1c) of over-chlorinated cyclohexylamine (amine:Cl molar ratio < 1) recorded at pH 2 shows what are assigned as the protonated forms of cyclohexylamine (*m*/*z* 100), *N*-monochlorocyclohexylamine (*m*/*z* 134, 136), and *N*,*N*-dichlorocyclohexylamine (*m*/*z* 168, 170, 172). Another important feature of this mass spectrum is the appearance of a product assigned to protonated *N*-chlorocycloheximine (*m*/*z* 132), presumably produced by HCl loss from protonated *N*,*N*-dichlorocyclohexylamine. Protonated cycloheximine, the dehydrohalogenation product of *N*-chlorocyclohexylamine, is observed to a relatively much smaller extent. Slow hydrolysis of the ketimine to cyclohexanone was also observed.

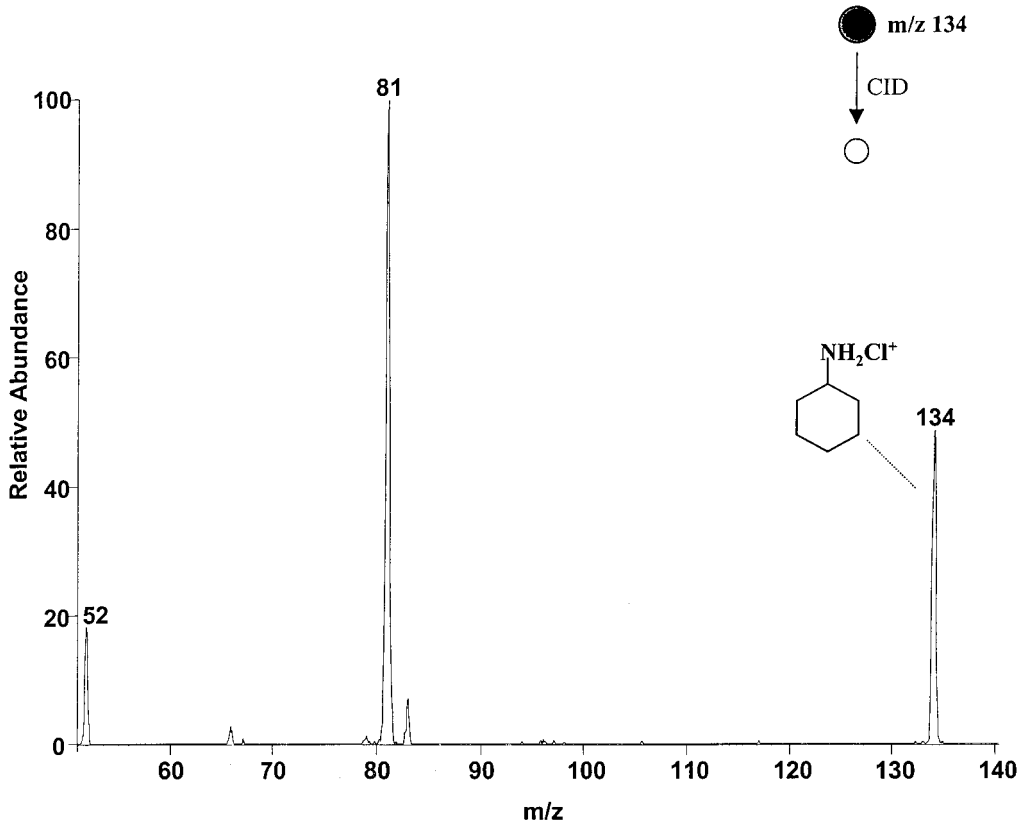

Figure 2. Positive ion APCI MS^2 spectrum of *N*-chlorocyclohexylamine generated at pH 6 from 1 mM cyclohexylamine (CHA) using 1 mM NaOCl. *N*-chlorocyclohexylamine (*m*/*z* 134) was isolated using a 10 Th window and 8% CID energy.

Structural elucidation of the ions identified in the ESI and APCI mass spectra was carried out by collision-induced dissociation (CID) and H/D exchange. Comparison with the CID behavior of authentic ions was also used in certain cases. Fragmentation of protonated *N*-chlorocyclohexylamine ion (*m*/*z* 134) is summarized in the MS/MS spectrum shown in Figure 2. Fragmentation occurs by loss of neutral NH_3 and HCl (producing an ion at *m*/*z* 81), or neutral cyclohexene loss (producing the ion at *m*/*z* 52). This behavior, together with the fact that H/D exchange shows that the ion contains two labile protons, parallels and confirms the assignment of the *m*/*z* 134/136 product as *N*-chlorocyclohexylamine. Similar considerations led to the identification of the other products shown in Scheme 1 using the CID and H/D exchange data. Hydrolysis to yield the ketone was confirmed by comparison of the CID behavior of the ion of *m*/*z* 99, mass-selected by APCI and isolated from the reaction mixture, with that of the authentic protonated molecule.

The ESI spectra of the cyclohexylamine chlorination product mixtures differ from the APCI spectra in that the dichloro derivative does not appear, but the imines occur in much lower abundance. This is the case over the entire pH range of 1−9. The chlorination pathway and associated reactions are proposed to occur as shown in Scheme 1. Evidence for the structures shown here came from tandem mass spectrometry and H/D exchange experiments, as already discussed.

Dichloramines were not detected by electrospray ionization, even at extremely low pH values (pH < 1) and high chlorine concentrations. According to Margerum and co-workers,[3] the first step in chlorination is electrophilic attack by Cl^+. Thus, in this case, a Lewis acid−base reaction occurs in which the acid is Cl^+, and the basic group is the amino nitrogen of the organic substrate. Protonated amino groups cannot function as Lewis bases, so the reactant must be the nonprotonated form. Thus, the relative reaction rates are determined by the degree of protonation (dependent on pH) and by the relative Lewis basicity of the amino group(s) in the system. It has been noted[17,18] that the proton affinities of chloramines decrease with increasing chlorination, and one may assume that this trend parallels that of the basicity in solution.

The above considerations account for the fact that the distribution of chlorination reaction products is dependent on the pH at which the reaction mixture is examined, as shown in Figure 3. At low pH values, the amino group is almost completely protonated, so the rate of chlorination is low. However, the reaction product (monochloramine) is a weaker base than the original amine; it is therefore protonated to a smaller extent, and the net rate of chlorination is higher for this compound. This phenomenon produces spectra of the type shown in Figure 1c in which the monochloramine is a transitional product generated only in low concentrations, because further chlorination to generate the dichloramine is favored. The end product of the reaction sequence is *N*-chlorocycloheximine, which is produced by HCl loss from the dichloramine. *N*-Chlorocycloheximine undergoes slow hydrolysis, producing cyclohexanone. The rate of hydrolysis is strongly enhanced by the elevation of pH. At higher pH values, the interplay between chlorine cation affinity (Lewis acidity of the amine) and pH results in only the amine being initially chlorinated; further chlorination of the monochloramine occurs only when there is no unreacted amine left in the system.

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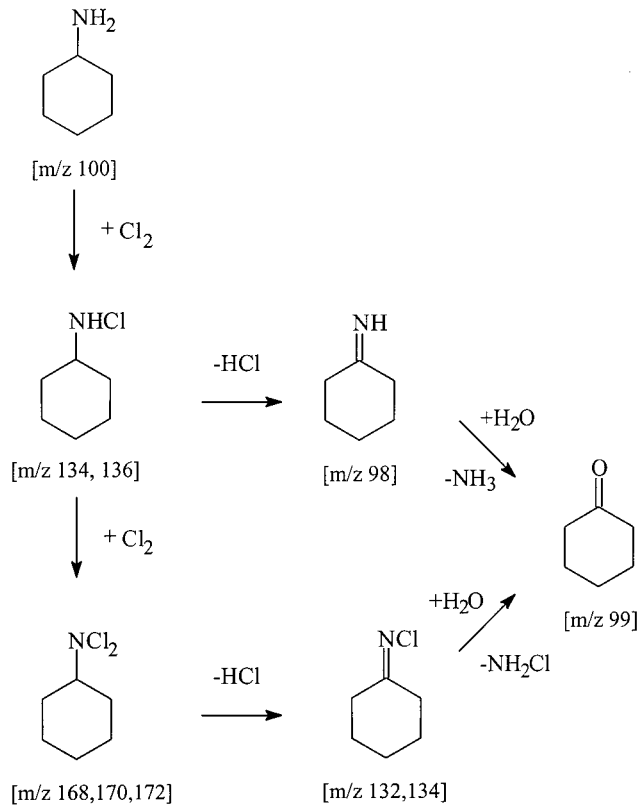
Scheme 1[a]



[a] m/z ratios are for protonated forms.

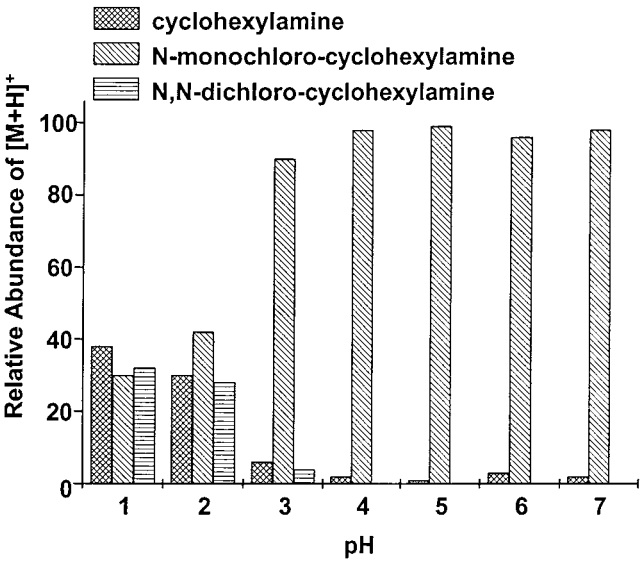


Figure 3. Distribution of cyclohexylamine and chlorinated cyclohexylamine derivatives as a function of pH. Equal quantities of pH-adjusted cyclohexylamine hydrochloride and NaOCl were mixed, and positive ion APCI spectra were acquired. At pH values above 3, only the expected *N*-chlorocyclohexylamine is present. At lower pH values, the relative rate of the second chlorination step is increased, leading to the formation of *N*,*N*-dichlorocyclohexylamine.

These considerations explain the overall trends observed in the experimental data. The simplest interpretation of the data is that the products of chlorination in solution are being observed in the ESI and APCI experiments with no effects due to differences in ionization efficiency. However, one cannot exclude the possibility that analogous ion/molecule reactions occur during the ionization process or that differences in ionization efficiency might skew the results.

Aliphatic α,ω-Diamines. The chlorination reactions of putrescine, a representative aliphatic diamine, are more complex than those of cyclohexylamine because of the multiple nucleophilic sites and the possibility of intramolecular elimination reactions. In addition to the main *N*-chlorination reaction sequence terminating in *N*,*N*,*N*′,*N*′-tetrachloroputrescine (Figure 4.), various side reactions occur, including imine formation by HCl elimination and intramolecular cyclization by ammonia (or inorganic chloramine) elimination. Imine formation in this case is not an end product, as indicated by the fact that various nitrile compounds are also observed. The degree of sequential chlorination is strongly pH-dependent in the range of pH 1−4. The propensity to intramolecular cyclization (via nucleophilic substitution) is determined by relative basicity (proton affinity) of the nitrogen sites: only nonprotonated nitrogen can act as a nucleophilic agent, and only protonated nitrogen acts as a leaving group. Therefore the *more* chlorinated nitrogen atom (corresponding to a lower pK_a of the conjugated acid, cf. the inorganic chloramines) acts as the nucleophile, and the higher pK_a less chlorinated amine is eliminated as the neutral inorganic chloramine. Once again, this discussion assumes that products of solution reactions are simply being sampled by the ESI/APCI ionization method. The degree to which this is true is a problem of continuing interest.[19]

The overall reaction scheme is summarized in Scheme 2. Evidence identifying the proposed ion structures was obtained by tandem mass spectrometry and H/D exchange experiments. Collision-induced dissociation of chlorinated putrescine ions is more complex than that of the monochloroamine. The general fragmentation pathway involves cyclization with associated elimination of neutral ammonia or an inorganic chloramine. An interesting feature of this gas-phase fragmentation pathway is that the less chlorinated nitrogen is eliminated, the same trend which occurs in the course of cyclization in the condensed phase. Information on the site of protonation comes from the MS/MS data, because the protonated site generally directs the amine that is eliminated. The cyclic structures were elucidated by H/D exchange and MS^3 experiments.

The ion at *m*/*z* 104/106 has no exchangeable protons, which is indicative of a quaternary ammonium cation. Assuming that the chlorine atom is bound to nitrogen, the only alternative structure would be an unlikely *N*-chlorobutyronitrile. (The MS/MS spectrum contains only one fragment ion at *m*/*z* 68, which does not give any further fragments in MS^3 in the mass range of *m*/*z* 50−70, excluding any open chain structures.) The ion at *m*/*z* 140/142/144 contains only one mobile proton, and CID yields the ion at *m*/*z* 104/106.

Stability of Ions in the Source and the Atmospheric Interface. An interesting feature of organic chloramines is the low stability of the protonated molecules in the mass spectrometer. Experiments suggest that the chloramines decompose at higher temperatures. For example, the abundance of the protonated *N*-chlorocyclohexylamine ion (ClCHA+H^+) dramatically decreases when the capillary is heated above 150 °C. Other parameters that

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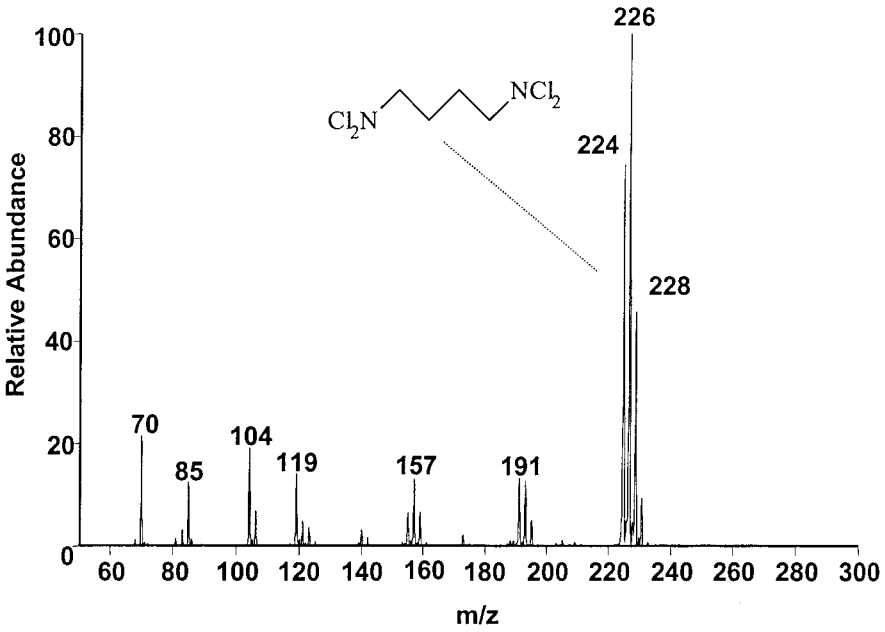


Figure 4. Positive ion APCI mass spectrum of over-chlorinated putrescine.

strongly affect ion intensity are the sheath and auxiliary gas flows. These observations seem to be due to the ease of dissociation of these ions, so that ion internal energies must be kept low in order for them to reach the analyzer intact. Because of this, experimental parameters were optimized to maximize the signal for *N*-chlorocyclohexylamine.

The results described above suggest that there is a decomposition process occurring, although localization of this process is difficult. The heated capillary interface might play a key role in thermal decomposition, and neutralization could occur on a metal surface. Collisions occurring in the gas phase could also be involved in the decomposition process. Because few fragment ions are observed in the mass spectra, dissociation appears not to be a major contributor.

Determination of Free Chlorine Content. The results obtained in the study of the model compounds suggest that it might be possible to add a sacrificial organic amine to a chlorinated water sample and to use it to determine the amount of free chlorine indirectly by measuring the amount of chloramine formed. The advantages of this indirect method are (i) the chlorinated organic compound is much more readily measured than the simpler analytes and (ii) there is no need for independent measurements on the various individual chlorinating agents. However, for this approach to be successful, the sacrificial reagent (the organic amine) must meet the following criteria:

(1) The compound must react with all free chlorine in aqueous media.

(2) Reaction of the selected compound with chlorine must be significantly faster than any subsequent oxidation or other secondary reaction.

(3) The compound should not be present in natural or other water that is to be measured, and if it is, its concentration will need to be measured before and after the addition of the sacrificial reagent.

(4) The chosen compound must not react with inorganic chloramines present in the water sample on the time-scale of the experiment.

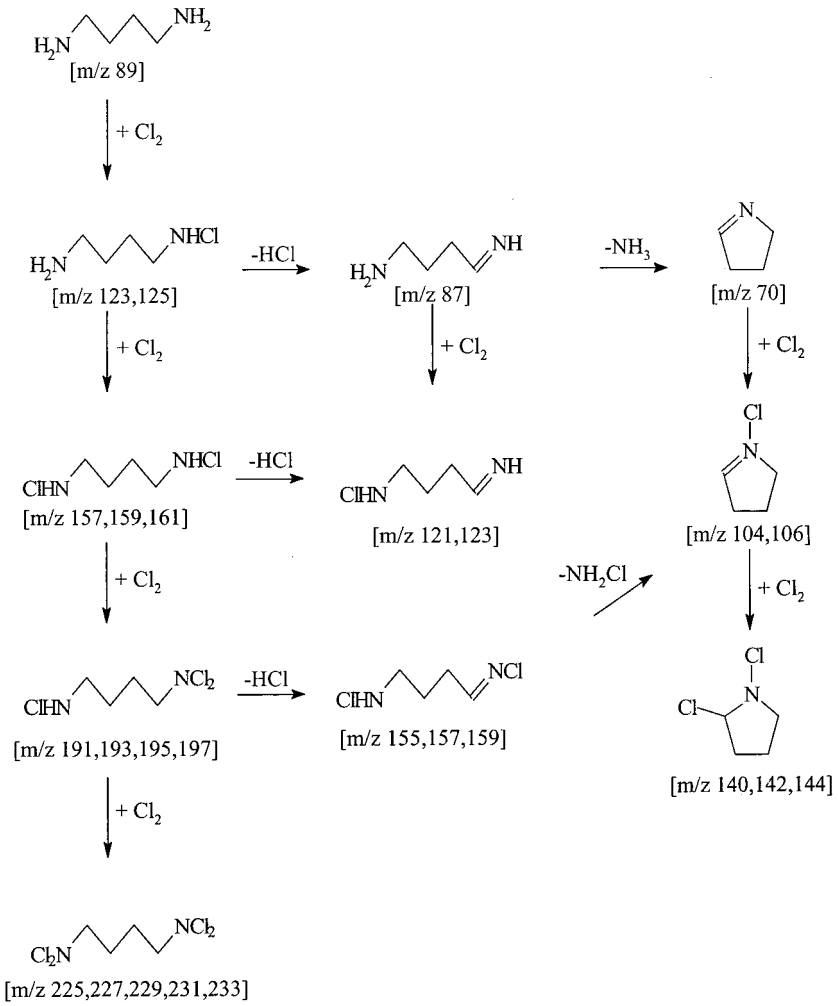
(5) The compound must not be hydrolyzed by water at pH 3−7.

Two model compounds (cyclohexylamine and methylamine), were selected and tested to see whether they satisfy the conditions listed above. Reaction with chlorine produces organic monochloramines in both cases, and both reactions are fast. The amount of byproduct formed is very low in the case of cyclohexylamine; only minor quantities of *N*,*N*-dichlorocyclohexylamine and *N*-chlorocyclohexanimine were observed (Figure 1a). Unfortunately, methylamine (and *N*-chloromethylamine) is oxidized by chlorinated water; presumably, the methyl group is oxidized to carbon dioxide via carboxylate. Thus, methylamine and *N*-chloromethylamine do not meet the second condition.

Cyclohexylamine reacts readily with free chlorine to give relatively stable products, as already indicated, meaning that it fulfills the first two criteria noted above. It is not detected in tap or natural water samples (the lower limit of detection was experimentally determined to be 10 μg L^{-1}), thereby fulfilling the third requirement. To establish whether cyclohexylamine reacts with NH_2Cl, a solution was treated with NH_2Cl and incubated for 24 h. The *N*-chlorocyclohexylamine concentration of the sample did not exceed the lower limits of detection (satisfying the fourth criterion). Finally, the fifth requirement was verified by measuring the stability of *N*-chlorocyclohexylamine: after 72 h, only 1−3% of the chloroamine had decomposed at pH 7, with less than 1% decomposition at pH 2.

Summarizing the results, cyclohexylamine fulfills all five of the conditions thought necessary for a compound to be considered as a sacrificial agent in the indirect determination of free chlorine in water. However, additional conditions must be met for this determination to form the basis for a good method of analysis. These include appropriate limits of detection (LOD),

Scheme 2[a]



[a] m/z ratios are for protonated forms.

Table 2. Comparison of ESI and APCI-MS Methods of *N*-chlorocylclohexylamine Determination with Titration

method	electrospray	APCI	titrimetry[a]
dynamic range	10^4-10^5	10^4-10^5	10^3
linear range	10^1-10^2	10^2-10^3	10^2
LOD, $\mu g\ L^{-}1$	2−200	5−40	1
RSD, %	1−20	2−10	1
matrix interferences	+++	+	++

[a] DPD/FAS.

linearity, linear dynamic range, and precision as measured by RSD.

Both ESI and APCI were tested in developing the method further and the results are compared in Table 2. APCI was found to yield lower LOD values, lower RSD, and to suffer fewer matrix interferences. Calibration curves were obtained for chlorinated DI water by adding 1 mM cyclohexylamine to standard water samples with free chlorine contents in the range of 0.01−10 mg L^{-1}

Deionized water, tap water, and wastewater effluent samples were collected from the West Lafayette Wastewater Facility in November (during which time the chlorination process is not in use). Comparisons of the limit of detection, linear dynamic range, linearity, and RSD for the deionized, tap, and wastewater samples are listed in Table 3. Although the matrix effects have not been extensively investigated at this stage, the following factors should be taken into account as the method is developed further: (1) The pH of the water sample not only influences the analyte of interest but affects all other contaminants in the sample. (2) Metals or other contaminants that sequester either free chlorine or amines could affect the results. (3) Species with proton affinities higher than the chlorinated sacrificial amine could raise the limits of detection.

CONCLUSION

The methodology and supporting analytical results shown in this paper demonstrate the applicability of APCI and ESI to study chlorination chemistry. The data on the measurement of *N*-chlorocyclohexylamine determination suggest that a simple yet sensitive method based on quantitation of the extent of chlorination of this compound could provide the basis for an on-line monitoring method for the quantitative analysis of free chlorine and organic chlorination byproducts. The data reported are taken using full-scan mass spectra, and if needed, improved sensitivity could be obtained using reaction monitoring to characterize this particular

Table 3. Matrix Dependence of Characteristic Features of the ESI- and APCI-MS Methods for Active Chlorine Quantification

	method					
	APCI			electrospray		
	deionized water	tap water	wastewater effluent	deionized water	tap water	wastewater effluent
LOD, ppb	5	20	40	2	50	200
linear range	10^3	10^2-10^3	10^2-10^3	10^3	10^2	10^1
linearity, R^2	0.999	0.993	0.998	0.999	0.984	0.998
RSD, %	2.4	5.5	4.1	1.7	9	9

compound in a complex sample. The dehydrochlorination dissociation reactions 134 → 81 and 136 → 81 should have value for the selective determination of chlorinated cyclohexylamine.

The strength of both of these ionization techniques lies in their capability to investigate a wide range of compounds (volatile to nonvolatile, polar to nonpolar) without the need for sample preparation. There are small differences in the APCI and ESI spectra and in the quantitative results (ie., LOD, linearity, and RSD). The APCI data are less dependent on the pK_a values of the compounds of interest in the aqueous phase, and matrix effects are not typically observed. ESI is more commonly used to investigate aqueous samples and is believed to be representative of the solution-phase chemistry. For both ionization methods, an unresolved question is whether particular reactions occur in the gas phase as well as the solution phase. Another interesting aspect of the work is the fragility of some of the chlorinated species studied; however, decomposition processes can be minimized by using appropriate instrumental parameters.

Insights into the chlorination reactions of typical organic amines and diamines are described. Byproducts are identified and evidence is provided for the ion structures proposed. Competition between chlorination by Cl^+ and protonation is a key to much of the observed chemistry.

The indirect method anticipated for active chlorine quantification is based on reaction of active chlorine with an amine followed by the quantification of the product. The main advantages of this approach are (i) the nature of the chlorinating agent need not be known, provided that it reacts with the chosen amine and (ii) the amine can be chosen so that its chlorination products are readily detected and quantified. Although this has not yet been demonstrated, it is likely that the amine could be chosen so as to be more or less reactive, that is, to have a greater or smaller Cl^+ nucleophilicity. In other words, by selecting the reagent, it should be a matter of choice as to which group of dissociable Cl-containing species are measured.

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