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Differentiation and Quantification of Free Chlorine and Inorganic Chloramines in Aqueous Solution by MIMS

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A membrane introduction mass spectrometric (MIMS) method for differentiation and quantification of free chlorine and inorganic chloramines in aqueous solution was developed based on a low-cost mass spectrometer. Several factors were examined for system optimization. Only membrane temperature and liquid flow rate exerted substantial influences on the performance of MIMS. Essentially linear response curves over several orders of magnitude of concentrations were observed, and limits of detection for free chlorine and mono-, di-, and trichloramine at 0.1, 0.1, 0.02, and 0.06 mg/L as Cl_2 , respectively, were demonstrated. System performance was evaluated with chlorination of ammoniacal water. Similar results were obtained by the MIMS method, conventional DPD/FAS titration, and UV–visible spectroscopy. Identification and quantification of inorganic chloramines by the MIMS method and DPD/FAS titration were also compared for chlorination of an aqueous solution containing glycine as the nitrogen source as well as samples of potable water and wastewater. These experiments demonstrated an advantage of MIMS relative to titration in that MIMS was able to unambiguously quantify and characterize the inorganic chlorine residual.

Introduction

Chlorination, applied as a treatment process for inactivating microorganisms present in aqueous solution, has been well-developed and practiced in municipal water and wastewater disinfection, swimming pool disinfection, and cooling water biofouling control. Although alternatives to chlorination, such as ozonation and UV irradiation, are being selected with increasing regularity, the ability of chlorination systems to develop a reasonably stable disinfectant residual ensures that chlorination will remain a predominant antimicrobial process for the foreseeable future.

Chlorination chemistry in the aqueous environment has been extensively studied, especially with regard to the chemistry of reactions between free chlorine and ammonia (1). In aqueous solutions, HOCl undergoes substitution and oxidation–reduction reactions with ammonia and organic-N compounds to form monochloramine (NH_2Cl), dichloramine (NHCl_2), trichloramine (NCl_3), and organic chloramines (2). However, tremendous variations in the microbiocidal efficacy of these compounds have been reported in the literature (3–5).

From the perspective of analytical chemistry, standard methods for residual chlorine and chloramine determination are listed in ref 6. However, it has been demonstrated that organic chloramines interfere with titrimetric determinations of free chlorine (7, 8) and cannot be differentiated from inorganic chloramines by either titrimetric or colorimetric methods (9). Additionally, other standard methods listed in ref 6 are of questionable validity in most chlorine-based disinfection applications because of the probable presence of sources of analytical interference, which can provide false positive signals by oxidation of indicator agents or by carrying electrical current (10). Alternative methods have been developed and published including derivatization/HPLC (11), membrane separation/spectrophotometric measurement (12), and a stopped-flow spectrophotometric method (13). These methods provide reproducible quantitative data but suffer from drawbacks: some of these methods include requirements for sample preparation, which can be time-consuming and may shift equilibria among chlorine compounds; other methods are not suitable for application to complex mixtures (such as wastewater).

Membrane introduction mass spectrometry (MIMS) has been used in many applications (14). The principles of the method can be found in ref 15. It has been rapidly developed in numerous applications recently because of the awareness of its advantages relative to other analytical methods. In this method, analytes generally do not require preconcentration or other workup prior to analysis. Analytes can be directly delivered to the membrane interface in an aqueous solution, permeate through the membrane, and reach the mass spectrometer while the majority of water is rejected (along with low-volatility solutes). MIMS has been proposed as an advantageous method for analysis of organic and inorganic chloramines in aqueous solution (16, 17). Qualitative identification of inorganic and organic chloramines by MIMS has been demonstrated previously.

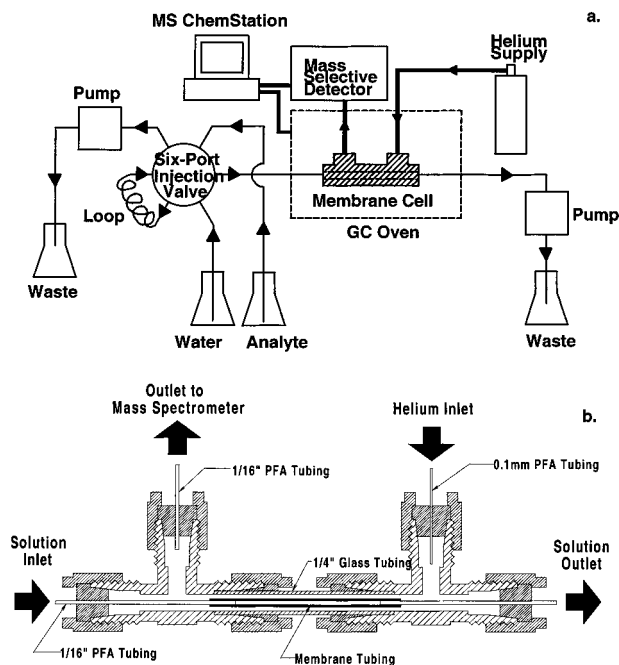
Experimental Procedures

Materials and Methods. In all cases, solutions were prepared from reagent-grade chemicals or stock solutions and diluted to target concentration from chlorine demand-free water (CDFW), which was prepared from nanopure water followed by double distillation.

Stock-free chlorine solution was prepared from 5% sodium hypochlorite (NaOCl), diluted to 4000–5000 mg/L as Cl_2 , and stored in aluminum foil-covered glass-stoppered flasks. The solution was standardized periodically by titrimetric methods (6). Free chlorine standard solutions were prepared by dilution with phosphate buffer (pH 7).

Monochloramine (NH_2Cl) standard solutions were prepared daily by mixing a free chlorine solution with an ammonium chloride (NH_4Cl) solution at a chlorine to ammonia molar ratio of 1.00:1.03 (12) and standardized titrimetrically. Both solutions were adjusted to pH 10 with sodium hydroxide (NaOH) prior to mixing. Dichloramine (NHCl_2) standard solutions were prepared by slowly pouring a free chlorine solution over an ammonium chloride solution at a chlorine to ammonia molar ratio of 1.80:1.00 for over 2 min while rapid stirring was provided (12). Both solutions were adjusted to pH 5 with acetic acid (1 M) prior to mixing. The concentration of dichloramine was titrimetrically standardized prior to each experiment after the solution sat overnight to complete the reactions. Standards of monochloramine/dichloramine for residual chlorine measurement experiments were prepared by slowly pouring a free chlorine solution over an ammonium chloride solution at a chlorine

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to ammonia molar ratio of 1.31:1.00 while rapid stirring was provided at pH 7 with phosphate buffer (0.01 M); these solutions were standardized spectrophotometrically (13) after 1 h. In this case, both monochloramine and dichloramine were relatively stable and abundantly present in solution. Standards of trichloramine were prepared following a similar technique but at a chlorine to ammonia molar ratio of 3.15:1.00, followed by titrimetric standardization. Trichloramine at low concentration (less than 2 mg/L as Cl_2) is relatively stable while all other chlorine species are present simultaneously. Concentrations of standards for residual chlorine measurement were prepared within a practical operational range (i.e., <10 mg/L as Cl_2).

System Setup. A Hewlett-Packard (HP) 5892 benchtop GC/MS, containing an HP 5972A single quadrupole mass selective detector (MSD), equipped with a computer control program (HP G1034C Software as the MS ChemStation) was modified to a MIMS configuration (Figure 1a). A remote membrane configuration was used due to the configuration of the GC interface for indirect heating of the ion source. The GC column was removed from the oven, and a flow-through membrane cell was installed. Analytes were introduced and delivered to the membrane cell via a Rheodyne 9010 injector to reduce flow disturbances. The membrane cell was constructed with a 1/4 in. o.d., 5 cm long glass tube with two T joints (Figure 1b). Medical/pharmaceutical silicon tubing (Baxter), which has become the default membrane material in MIMS systems, 0.25 mm i.d., 0.47 mm o.d., 60 mm long (contact length), connected with 1/16 in. o.d. tubing, was placed in the center of the membrane cell. The characteristics of this tubing and the principles of analyte transport and separation are defined in ref 15. A flow restrictor made from 0.1 mm i.d., 1 m long tubing was connected at the branch outlet of one T joint to deliver helium gas to the membrane cell and to maintain the vacuum in the ion source chamber (10^{-5} Torr). The 1/16 in. o.d. tubing, connected at the branch of another T joint, was used to transfer permeates with helium carrier gas to the ion source. All tubing, ferrules, and joints that came into contact with analytes were Teflon PFA or stainless steel to limit reactions and corrosion. The liquid/gas flow was operated in a counter-current manner so that maximum mass transfer could be achieved. System control,

tuning, data acquisition, and data analysis were managed with the MS ChemStation.

The system was operated under electron impact (70 eV) ionization. Mass spectra scan mode (35–125 amu) was used to evaluate chlorine speciation while selected ion monitoring (SIM) mode was used for quantification of specific compounds. The system was operated at optimum conditions, unless otherwise noted.

Procedures. The determination of residual chlorine by MIMS was based on the linear response of average steady-state abundance of selected ions (after background subtraction) to concentrations of chloramines. The system was pumped with CDFW until it reached a stable background. Standards of monochloramine/dichloramine and trichloramine were first continuously introduced to the MIMS system in a stepwise manner so that calibration curves were established. Molecular ions at m/z 53 ($\text{NH}_2\text{37Cl}^+$), 87 ($\text{NH}^{35}\text{Cl}^{37}\text{Cl}^+$), and 119 ($\text{N}^{35}\text{Cl}_3^+$) were selected for the monitoring of mono-, di-, and trichloramine, respectively. Samples of unknown composition were then introduced to the MIMS system in the same manner as the standard solutions to obtain abundance responses for the selected ions. Adjustment of pH with phosphate buffer was required for samples that were not the same as the pH of standards. The concentrations of inorganic chloramine compounds in the samples were estimated by comparison of measured abundance with the corresponding standard curve. Two drops (0.1 mL) of 2 M ammonium chloride solution were then added to 10 mL of the sample to convert free chlorine to monochloramine in solution. The modified solution was then introduced to the MIMS system in the same manner as described above. The concentration of free chlorine was estimated from the difference in monochloramine concentration between these two measurements.

Description and Handling of Potable Water and Wastewater. Unchlorinated samples from the Purdue University Potable Water Facility (West Lafayette, IN) were examined; this groundwater-based water supply has chemical characteristics that are typical of many municipal potable water supplies. Unchlorinated wastewater samples were used due to their complex chemistries and the potential for interference by inorganic and organic constituents. Samples from the Lafayette (IN) Sewage Plant (unnitrified) and the West Lafayette (IN) Municipal Wastewater Treatment Plant (nitrified) were selected to simulate wastewater effluents characterized by high and low ammonia content, respectively. Samples were collected in the unchlorinated form and transferred to the laboratory within 30 min prior to experiments to minimize changes of the constituents. The concentrations of ammonia and total organic nitrogen were measured with an ammonia ion selective electrode and the Kjeldahl digestion procedure. Both methods were carried out using the procedures defined in ref 6.

Potable water and wastewater samples were subjected to chlorination by the addition of 1.0, 5.0, and 10.0 mg/L NaOCl (as Cl₂). Chlorinated samples were subjected to analysis by DPD titration and MIMS 30 min after chlorine addition.

Results and Discussion

System Optimization. The performance of the MIMS system for residual chlorine determination was optimized based on the concentration/response behavior of selected ions. Selected ions were determined by operation of the system in scan mode ($35 \leq m/z \leq 125$). Figure 2 presents the spectra of free chlorine and inorganic chloramines by introduction of high concentrations of standards of mono-, di-, and trichloramine to MIMS. These standards were prepared as described previously. The spectra agreed well with the possible molecular ions and fragments predicted by calculation. Although the standards were prepared in conditions

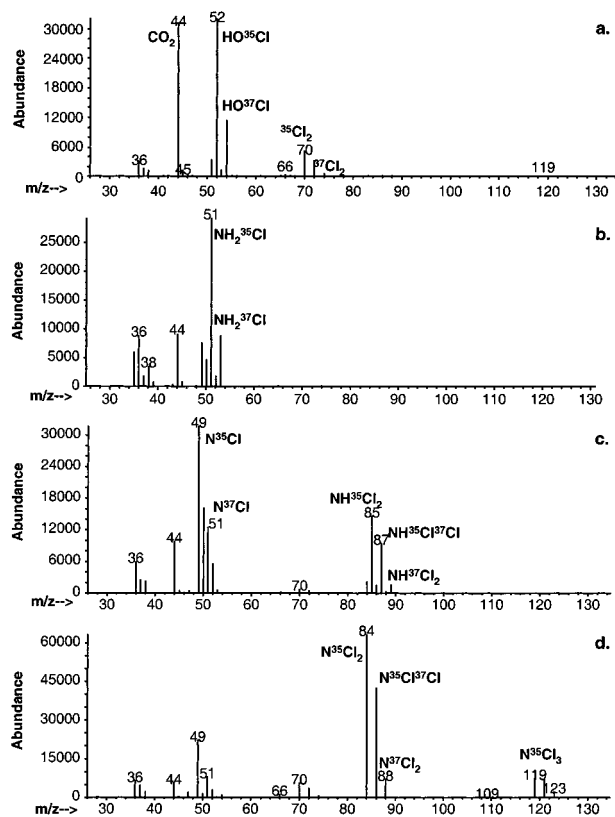


FIGURE 2. Representative EI mass spectra ($35 \leq m/z \leq 125$) of (a) free chlorine (2000 mg/L as Cl₂), (b) monochloramine (40 mg/L as Cl₂), (c) dichloramine (20 mg/L as Cl₂), and (d) trichloramine (20 mg/L as Cl₂).

favorable to the formation of the assigned chloramine, small peaks attributable to other chloramines were found in Figure 2b–d because of the unavoidable equilibria between the inorganic chloramines. The peak at m/z 44 present in Figure 2 is believed to be attributable to the formation of CO₂ by the reaction between +1 valent chlorine and trace amounts of organic carbon in the water. Peaks at m/z 51, 52, and 53 in Figure 2a,b represent a source of interference in the differentiation of free chlorine (as HOCl) and monochloramine by MIMS. However, further investigation demonstrated that free chlorine (HOCl) introduced to the system at aqueous concentrations of practical significance in disinfection operations (less than approximately 10 mg/L as Cl₂) did not yield quantifiable ion abundance at m/z 52 and 54 and no peak at m/z 53 and 51 at neutral pH. Therefore, determination of monochloramine was not interfered with by the presence of free chlorine; these results also demonstrated that direct measurement of HOCl is not practical using this MIMS configuration. Additionally, m/z 51 cannot be used as a selected ion for monochloramine quantification because all inorganic chloramines were found to yield this ion; therefore, m/z 53 was selected for monochloramine determination. Dichloramine yielded unique, strong peaks that could be selected for dichloramine determination at m/z 85, 87, and 89 (see Figure 2c). Trichloramine yielded strong peaks at m/z 84, 86, and 88 (see Figure 2d); however, the dichloramine peaks represent a potential source of interference in trichloramine quantitation (see Figure 2c). Therefore, only the peaks at m/z 119, 121, and 123 could be selected for trichloramine determination.

Factors such as membrane temperature, mass spectrometer temperature, gas and liquid flow rates, pump types, and flow configuration (flow over or flow through) were evaluated in a matrix to obtain the optimum conditions for residual chlorine measurements (as characterized by shortest re-

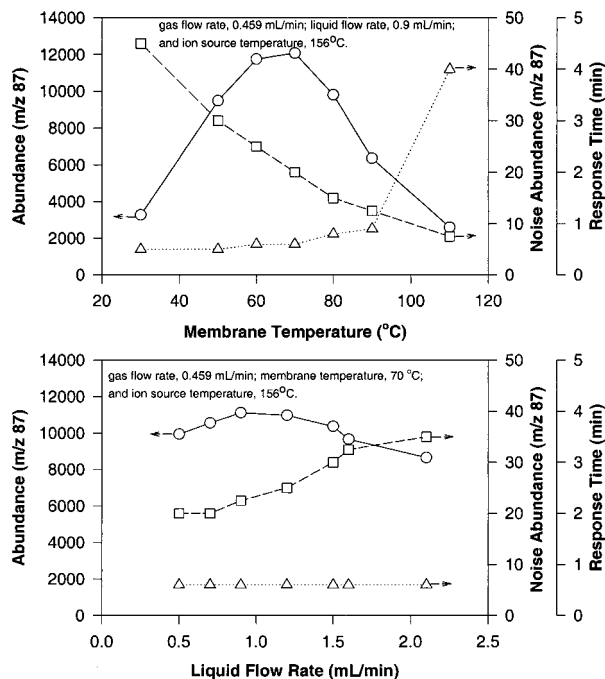


FIGURE 3. Effects of membrane temperature and liquid flow rate on the MIMS system performance (dichloramine at 9.2 and 8.5 mg/L as Cl₂, respectively): ○, signal abundance; □, signal response time; △, signal noise.

sponse times, largest response, and lowest noise). For these experiments, aqueous solutions containing monochloramine at a concentration of approximately 10 mg/L (as Cl₂) and dichloramine at a similar concentration were introduced to the system as reference compounds. The results showed that membrane temperature and liquid flow rate were important factors in determining system performance (Figure 3). Other system characteristics had little effect on performance. The system yielded the largest abundance at membrane temperature between 60 and 70 °C. For membrane temperature below this range, an increase in temperature resulted in increasing diffusivity and permeability through the membrane interface, so that higher abundance and lower signal response time were achieved while slightly increasing noise in the signal. However, the steady-state abundance dramatically decreased at temperature above this range, presumably due to the approach to the boiling point of water and the concomitant increase in permeation of water through the membrane. These temperature increases were also accompanied by substantial noise.

Liquid flow rate also had a profound influence on system performance. The system reached the maximum signal abundance at a liquid flow rate of 0.7–1.0 mL/min. The signal response time increased with flow rate, while signal noise was largely unaffected. Other factors, as mentioned above, did not have substantial influence on system performance. Flow configuration (flow over or flow through) also did not affect system performance if the same approach flow velocity was employed. Similar results were observed when experiments were performed with monochloramine.

Performance optimization was evaluated by allowing only one process variable to change, while all others were maintained at constant values from each of these experiments (i.e., synergistic effects of system parameters were not evaluated). Optimum conditions for quantification of chloramines using this MIMS configuration were as follows: gas flow rate at 0.459 mL/min, liquid flow rate at 0.9 mL/min, membrane temperature at 70 °C, and ion source temperature at 156 °C resulting a response time of approximately 2 min.

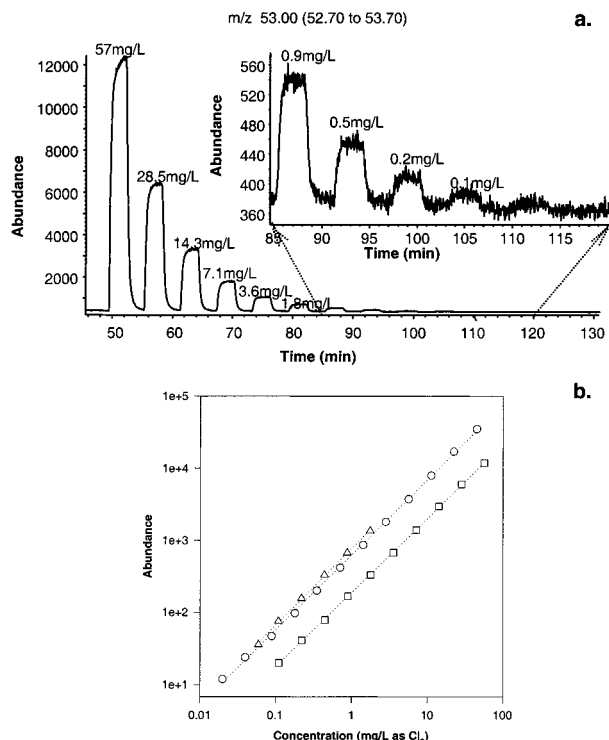


FIGURE 4. (a) Quantification of monochloramine by the MIMS method at $m/z = 53$: concentrations refer to titrimetrically determined values (as Cl₂) up to the limit of detection (see insert). (b) Linear response curves of the MIMS method for chloramines: □, monochloramine ($m/z = 53$); ○, dichloramine ($m/z = 87$); △, trichloramine ($m/z = 119$).

Analytical Performance. Under the optimum condition described above, a standardized monochloramine solution at known concentration was diluted serially and introduced in a stepwise manner to obtain both the calibration curves and limits of detection. Figure 4a represents the output for a typical experimental run using monochloramine. Similar results were obtained from experiments performed with standardized dichloramine and trichloramine solutions. The limits of detection of mono-, di-, and trichloramine, based on a signal-to-noise ratio of 2, were 0.1, 0.02, and 0.06 mg/L as Cl₂, respectively. Figure 4b illustrates typical calibration curves for all three chloramines. Essentially linear response curves over several orders of magnitude of chloramine concentration were observed. The calibration curve and the limit of detection for free chlorine were the same as monochloramine since free chlorine was completely converted to monochloramine in the ammonification step.

Measurements of Chlorine Residuals. The performance of the system for residual chlorine determination was evaluated by analysis of aqueous solutions containing ammonia after chlorination. Experiments were performed in well-mixed glass-stoppered flasks in the dark. For each experiment, 1.0 mL of stock ammonia solution (100 mg/L as N) was added to 200 mL of 0.01 M phosphate buffer solution (pH 7.0) to achieve an ammonia concentration of 0.5 mg/L as N. Aliquots of standardized free chlorine stock solution were then added to the flasks. The experiments were repeated for chlorine:nitrogen mass ratios of 2.0–16.0 at regular intervals of 2. Concentrations of chlorine residuals were determined 30 min after chlorine addition by DPD/FAS titration and the MIMS method.

Figure 5a presents the results of chlorine residual determinations by DPD/FAS titration and the MIMS method after 30 min of chlorination of an aqueous ammonia solution. The typical "breakpoint chlorination" curve shape was

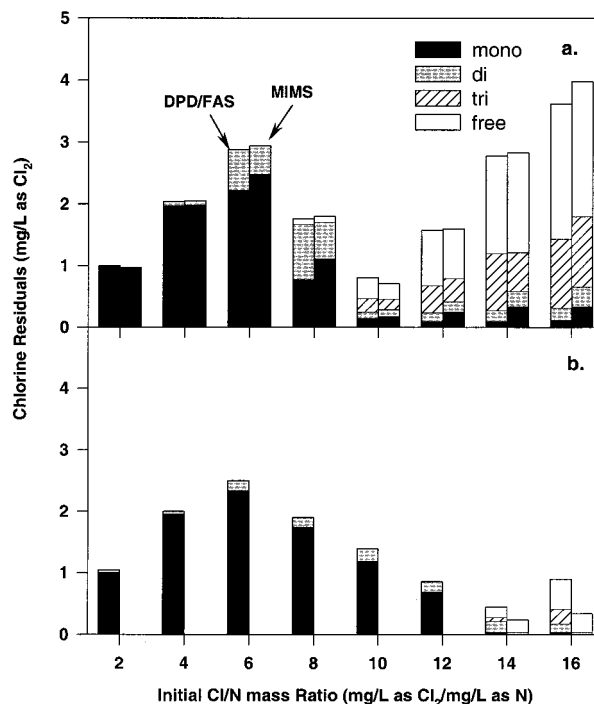


FIGURE 5. Residual chlorine concentrations as a function of Cl:N mass ratio after 30 min chlorination of an aqueous solution containing (a) ammonia and (b) glycine (0.5 mg/L as N) at pH 7. For each Cl:N ratio, residual chlorine was measured by DPD/FAS titration (left bar) and MIMS/EI (right bar).

evident in the results from both methods. In quantitative terms, results from both methods showed fairly good agreement, especially in the "chloramination" portion of the curve (low Cl:N ratios). However, at higher Cl:N ratios, when monochloramine and dichloramine both abundantly existed in solution, results of the MIMS method tended to indicate a higher proportion of monochloramine than the results of DPD/FAS titration. The concentrations of monochloramine and dichloramine were further confirmed spectrophotometrically (13). Results obtained spectrophotometrically were in agreement with values obtained by the MIMS method. These results suggest that MIMS may more accurately represent inorganic chloramine speciation than DPD/FAS titration, probably due to ambiguity in the titrimetric procedure in terms of completion of the reaction between monochloramine and iodide (6). Nevertheless, the total concentration of combined chlorine determined by these three methods agreed well in all cases.

A similar experiment was conducted with glycine as the source of nitrogen. Glycine was selected as a "model compound" for representation of organic-N because it represents a simple amino acid and is commonly found in natural water (18). The results of this experiment are summarized in Figure 5b. The characteristic breakpoint curve shape was evident in the data from DPD/FAS titration. The data from MIMS analysis show a distinctly different character, especially in the region where the residual is expected to be dominated by chloramines (low Cl:N ratios). Conyers and Scully (19) demonstrated that chlorination of amino acids resulted in a series of substitution and oxidation-reduction reactions that are qualitatively similar to those that resulted from chlorination of ammoniacal solutions.

These data illustrate an important advantage of MIMS in quantification of chlorine residuals, namely, the ability to differentiate among organic and inorganic forms. The lack of this ability in conventional DPD/FAS titration represents an important limitation of this method, in that organic

TABLE 1. Comparison of Residual Chlorine Measurement in Samples of Wastewater and Water^a

chlorine dose	species	residual chlorine							
		West Lafayette wastewater (NH ₄ ⁺ -N, 0.04 mg/L; org-N, 0.85 mg/L)				Lafayette wastewater (NH ₄ ⁺ -N, 12.2 mg/L; org-N, 13.1 mg/L)		Purdue potable water (NH ₄ ⁺ -N, 0.05 mg/L; org-N, 0.35 mg/L)	
		DPD		MIMS		DPD		DPD	MIMS
		mean	RSD ^b (%)	mean	RSD ^b (%)				
1.0	free	0		0		0	0	0.38	0.13
	mono	0.12	4 (<i>n</i> = 6)	0		0.08	0.07	0.09	0
	di	0.05	12 (<i>n</i> = 6)	0.03	2 (<i>n</i> = 6)	0.04	0.02	0.02	0
	tri	0		0		0	0	0	0
5.0	free	0.16	14 (<i>n</i> = 6)	0.17	5 (<i>n</i> = 6)	0.16	0	4.28	3.22
	mono	0.15	17 (<i>n</i> = 6)	0		1.94	2.05	0.14	0.26
	di	0.40	2 (<i>n</i> = 6)	0.22	1 (<i>n</i> = 6)	0.08	0.03	0	0.02
	tri	0		0		0	0	0.04	0
10.0	free	2.92	2 (<i>n</i> = 3)	2.58	1 (<i>n</i> = 3)	0.16	0	9.00	7.33
	mono	0.15	15 (<i>n</i> = 3)	0.13	5 (<i>n</i> = 3)	4.64	5.17	0.20	0.56
	di	0.77	8 (<i>n</i> = 3)	0.37	0 (<i>n</i> = 3)	0.40	0.24	0	0.05
	tri	0		0.08	3 (<i>n</i> = 3)	0	0	0.04	0.03

^a All analyses were conducted 30 min after sample chlorination. Chlorine concentration in mg/L as Cl₂. ^b Relative standard deviation (RSD) = standard deviation/mean.

chloramines are generally regarded as being minimally effective as disinfectants. The superior selectivity of the MIMS method, which is based on the mass-to-charge ratio of compounds, eliminates false measurements of organic chloramines as residual inorganic chloramines (Figure 5b). In particular, little or no residual inorganic chlorine was detected by MIMS up to a Cl:N mass ratio of 12. The "breakpoint" in chlorination of glycine appears at a higher Cl:N ratio than in chlorination of an ammoniacal solution; it is hypothesized that this shift in the breakpoint is attributable to other (unspecified) reactions between chlorine and glycine. Similar results have been reported previous by others (7, 8). The small amount of dichloramine (0.04 mg/L as Cl₂) observed in the MIMS measurements conducted on aqueous glycine solutions beyond the Cl:N mass ratio of 12 is hypothesized to be attributable to the formation of dichloramine following decomposition of chloro-organic-N compounds.

Application of MIMS to Potable Water and Wastewater Samples. The MIMS method was also evaluated with chlorinated drinking water and wastewater samples. Table 1 provides a summary of the chlorine residual measurements after 30 min of chlorination based on the MIMS method and DPD/FAS titration; these data are accompanied by measurements of NH₄⁺-N and organic nitrogen.

In most cases, the results from both procedures yielded comparable results. The data in Table 1 indicate a tendency for residual chlorine concentration estimates by DPD/FAS titration to be higher than those by MIMS, although exceptions to this trend are evident. These findings are qualitatively similar to those of Derrigan et al. (10) in which DPD/FAS generally yielded higher estimates of residual chlorine concentration than other methods when applied to chlorinated wastewater samples. Among the wastewater samples, the consistent trend of DPD/FAS to yield higher estimates of dichloramine than MIMS suggests the possible formation of dichloro-organic-N compounds.

To further characterize the behavior of the MIMS system for measurement of residual chlorine compound concentrations, the analyses by DPD/FAS and MIMS on the West Lafayette wastewater samples were replicated several times at all chlorine doses using the same wastewater sample. In all cases, the MIMS measurements were found to be more repeatable (lower RSD) than those of the titrimetric method.

Because high concentrations of ammonia were used in conversion of free chlorine to monochloramine (for quan-

tification of free chlorine), it was found that residual ammonia from this step could represent a source of interference in subsequent analysis. This source of interference was eliminated by thorough washing of the liquid transfer tubing with aqueous solutions of free chlorine followed by CDFW washing to remove residual ammonia and chlorine contamination.

The data presented in Table 1 reveal several characteristics that cannot be explained on the basis of chlorine–ammonia interactions. These discrepancies are most evident in the samples collected from the West Lafayette Wastewater Treatment facility. For example, the MIMS data for the West Lafayette samples indicate the presence of free chlorine and dichloramine at a chlorine dose of 5 mg/L (as Cl₂), while the samples subjected to a dose of 10 mg/L (as Cl₂) yield free chlorine and all three inorganic chloramine compounds. The West Lafayette MIMS data also indicate chloramine yields that exceed the initial molar concentration of ammonia present in the samples. Furthermore, for the chlorine: ammonia molar ratios used in the West Lafayette samples, conventional chlorine–ammonia chemistry would suggest a solution chemistry to be dominated by free chlorine, with trace quantities of NCl₃.

A number of possible explanations may be put forward regarding these discrepancies. First, the ammonia-N concentrations for the West Lafayette facility were close to the limit of detection for the ion selective electrode method. Second, the vast majority of the reactive nitrogen in these samples was present in the form of organic nitrogen. While some similarities may exist between chlorine–ammonia and chlorine–organic-N interactions, some important differences are also known to exist. For example, Conyers and Scully (19) have shown that chlorine–amino acid interactions can yield substantial quantities of ammonia, thereby augmenting the initial ammonia-N concentration. Third, the MIMS method relies on detection of ions or molecular fragments with specific *m/z*. Given the complexity of the aqueous mixtures that represent wastewater effluents and potable water supplies, it is possible that compounds could be present that may yield charged particles that coincide with the *m/z* ratios used to quantify residual chlorine compounds in this study. Though this potential for interference cannot be eliminated, its effects can be minimized by subtraction of the signal from an unchlorinated sample and by examination of the isotopic ratios of the compound of interest (e.g., abundance ratio of 9:6:1 expected for the peaks corresponding to dichloramine at *m/z* 85, 87, and 89, respectively).

Collectively, these findings illustrate some potential shortcomings of the MIMS method for quantification of chlorine residuals in environmental samples, although these limitations do not appear to be as severe as those that are known to exist for conventional titrimetric methods. Experiments based on chlorination of simplified solution matrixes may be expected to shed some light on these issues.

Acknowledgments

The authors are grateful to the Purdue Research Foundation for financial support of this research.

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Received for review November 23, 1998. Revised manuscript received April 14, 1999. Accepted April 16, 1999.

ES9812103