Determination of active chlorine in air by bonded phase sorbent collection and spectrophotometric analysis

The Analyst

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The development and application of a collection method for total combined gas-phase active chlorine (*i.e.*, Cl_2, HOCl and chloramines) based on a sulfonamide-functionalized silica gel sorbent are presented. Preparation methods for the sorbent are described, as are procedures for chemical and physical characterization, such as chlorine capacity and chlorine collection efficiency. For determination of the collected chlorine, a modified version of the *N,N′*-diethyl-*p*-phenylenediamine (DPD) colorimetric method was employed, which yielded a detection limit of 0.1 μg of chlorine. At flow rates ranging from 31 to 294 ml min^{-1}, the collection efficiency was > 90% based on breakthrough analysis. Recovery of chlorine spikes from 0.05 g aliquots of the sorbent was not quantitative (~ 60%) but was reproducible; the recovery is accounted for in samples by adding weighed amounts of sorbent to the standards. Analytical data for active chlorine concentrations (*i.e.*, Cl_2 + HOCl) above a swimming pool are presented.

Introduction

Chlorine and hypochlorites have many uses as oxidizing and disinfecting agents in industrial and other occupational environments (*e.g.*, water treatment facilities).[1] Monitoring of gas-phase chlorine is important in occupational environments owing to the adverse health effects associated with both acute and chronic exposure.[2] More recently, there has been considerable interest in the chemistry of Cl_2 and HOCl in the marine troposphere.[3,4] It is believed that chlorine atoms resulting from photolysis of Cl_2 and/or HOCl could be important oxidants in these marine environments.[5]

A number of different methods for the determination of gas-phase chlorine are available but few are generally applicable; most methods have drawbacks in terms of either sensitivity or selectivity. A method based on collection on a silver membrane, followed by release of the chlorine as chloride ion by reaction with $Na_2S_2O_3$ solution and analysis of the chloride by ion chromatography, has been reported.[6] However, this method cannot distinguish between the active chlorine species (Cl_2, HOCl and chloramines) and HCl. Methods based on the chloride specific ion electrode lack sensitivity and cannot distinguish Cl_2 from HOCl.[7] Derivatization reactions between Cl_2 and KBr–acetanilide reagent[8] and a 2,6-dimethylphenol–NaBr–H_2SO_4 mixture coated on silica gel[9] yield halogenated products that can be determined fairly sensitively and selectively by chromatography (GC or HPLC), but sample preparation, work-up and analysis times are fairly lengthy. A chemiluminescence method based on the reaction of OCl^- with H_2O_2 has been incorporated into a continuous monitor for gas-phase chlorine,[10] but the limits of detection were only in the ppm range.

For background tropospheric measurements, a tandem mass spectrometric technique has been used to collect some preliminary measurements.[11] An acid mist–alkaline mist collection procedure with ion chromatographic detection has also been developed, with characterization of HOCl collection efficiency[12] and some tropospheric measurements[13] having been performed. The former method is difficult to calibrate and to use in the field (*e.g.*, a 30% loss of Cl_2 occurs during sampling), while the latter does not completely distinguish between HCl, Cl_2 and HOCl and detection is limited by a high blank, since the detected analyte is chloride ion.

Chemistry of sulfonamides

The homogeneous liquid-phase reaction of sulfonamide compounds (and their *N*-alkyl-substituted derivatives) with active chlorine has been long known.[14] For example, the reaction of *N*-methylpropanesulfonamide with hypochlorous acid proceeds as follows:

$$CH_3CH_2CH_2SO_2NHCH_3 + HOCl \longrightarrow CH_3CH_2CH_2SO_2NClCH_3 + H_2O \qquad (1)$$

If the sulfonamide were reacted with Cl_2 instead of HOCl, the side product would be HCl instead of H_2O, thus potentially allowing discrimination between HOCl and Cl_2 (this possibility was not explored in this reported work). The reaction is thermodynamically favorable, and the *N*-chlorosulfonamide product retains oxidizing and biocidal properties similar to those of chloramines. However, whereas chloramines are not sufficiently stable to be isolated in pure form, *N*-chlorosulfonamides (and *N*-chloro-*N′*-alkylsulfonamides) can be isolated in pure form and are even available commercially [*e.g.*, as chloramine-T, which is *N*-chloro-4-toluenesulfonamide sodium salt, and halazone, which is 4-(*N,N′*-dichlorosulfamoylbenzoic acid]. Furthermore, the stoichiometry of *N*-chlorosulfonamides is very predictable and reproducible, unlike the case for chloramines; used as an oxidizer, the chlorinated sulfonamide regenerates the original sulfonamide and creates a chloride ion (*i.e.*, a two-electron oxidation, the same as the HOCl that generated the sulfonamide).

The utility of such a reaction in solution is fairly limited, but incorporating the chemistry on a surface medium creates new possibilities. Immobilization of the sulfonamide group on a polystyrene resin[15,16] creates a versatile class of materials that can strip active chlorine from aqueous solution,[14] can supply active chlorine upon demand (*e.g.*, for biocidal water treatment),[17] and can be used to conduct chemical reactions.[18,19] These materials (called Haloscrubs) are also effective at removing active bromine from water[14] and, once reacted to capacity, can be regenerated with reducing agents such as

HSO_3^- and N_2H_4.[17] The reaction with active chlorine or bromine is highly selective; apart from a reaction with HNO_2 to form a nitroso compound, few interferences are known.[17] The Haloscrubs are very stable and can be stored 'on the shelf' without special precautions.

The Haloscrubs were designed for application in aqueous systems; it was desired to extend the use of immobilized sulfonamide groups to the gas-phase collection of chlorine. For ease of handling and the possibility of increased collection efficiency due to increased surface area, it was considered desirable to change the supporting substrate from a polystyrene resin to silica. In the current work, realization of the concept was demonstrated, although speciation of individual active chlorine compounds was not attempted. Preparation, characterization and collection experiments are described below.

Experimental

Preparation of sulfonamide sorbent

Description of preparation. A silica surface (*e.g.*, silica gel) is reacted with 3-aminopropyltriethoxysilane or 3-aminopropyltrimethoxysilane (APTS) (Huls Petrarch, Bristol, PA, USA) to produce a propylamine-derivatized surface.[20] The amine groups are then reacted with methanesulfonyl chloride (Aldrich, Milwaukee, WI, USA) in the presence of an aprotic base [*e.g.*, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (Aldrich)] to produce the sulfonamide-derivatized surface [eqn. (2)]. Similar preparations have been exploited previously for modifying poly(styrene–divinylbenzene) cation exchange resins into sulfonamide-containing resins,[14–16] but have not previously been used to modify silica substrates.

$$\dashv\!)\mathrm{Si} - CH_2CH_2CH_2NH_2 + CH_3SO_2Cl \rightarrow \dashv\!)\mathrm{Si} - CH_2CH_2CH_2NHSO_2CH_3 + HCl \qquad (2)$$

Method. A 1.75 g aliquot of APTS is added to 120 ml of dry toluene (Aldrich; distilled) in a 500 ml Teflon beaker; the mixture is heated to 80 °C with stirring. A 50 g amount of chromatographic grade silicic acid (100 mesh; Aldrich) is added to the mixture and stirring and heating are continued for 30 min. If isolation of the amino-functionalized silica gel is desired, the beaker contents are cooled to room temperature, the remaining bulk solution is decanted and the remaining traces of solvent are removed *via* rotary evaporation and oven drying at 60 °C. The amino-functionalized silica gel is then washed with an excess of high purity water, then again oven dried at 60 °C.

To prepare the sulfonamide-functionalized gel, a 2:1 molar excess (*i.e.*, 1.6 ml) of methanesulfonyl chloride is added directly to the silica gel–solvent mixture (*i.e.*, isolation and rinsing are not required), along with 1.5 ml of DBU. The mixture is allowed to react at 80 °C for 30 min with stirring. The sulfonamide-functionalized silica gel is then washed and dried in the same manner as the amino-functionalized gel. Both dried functionalized silica gels are stored in a desiccator.

Characterization of sulfonamide sorbent

Chlorine capacity. To measure total chlorine uptake from solution, an excess of standard chlorine solution was added to a weighed amount of gel and mixed to allow complete reaction; the aqueous solution was decanted. The gel was then rinsed with distilled water and the rinsate combined with the original decanted liquid; the chlorine in the solution (representing the unreacted excess) was determined by titration with standard ferrous ammonium sulfate (FAS) (VWR, Los Angeles, CA, USA) solution with *N,N'*-diethyl-*p*-phenylenediamine (DPD) (VWR) indicator.[21] A stock standard chlorine solution was prepared by mixing 2.7 ml of commercial bleach (5.25% w/w NaClO) and 1.2 ml of glacial acetic acid (Spectrum, Gardena, CA, USA) in 1 l of water to make a solution of nominally 100 ppm chlorine (as Cl_2) at about pH 7; the solution was standardized daily *via* the FAS method. Working standard solutions for constructing calibration curves were prepared by serial dilution of the stock standard solution.

Direct measurement of bound active chlorine was accomplished by reacting a weighed amount of sulfonamide-functionalized gel with an excess of chlorine, as for the chlorine uptake measurements. After the solution had been decanted, the gel was washed with high-purity water (18 MΩ cm) (Barnstead, Dubuque, IA, USA) until the washings contained negligible amounts of chlorine and chloride. The gel was then transferred into a calibrated flask with water and an excess of hydrazine hydrate (85%) (Fisher, Pittsburgh, PA, USA) and diluted to volume. An aliquot of this solution was syringe filtered, diluted 100:1 and analyzed for chloride content by ion chromatography. The ion chromatograph used was a Dionex (Sunnyvale, CA, USA) Qic instrument, using an AS4A column, a 1.7×10^{-3} M $NaHCO_3$–1.8×10^{-3} M Na_2CO_3 eluent and a Milton Roy (Philadelphia, PA, USA) ConductoMonitor III conductivity detector in combination with eluent conductivity suppression.

Chloride concentration in chlorine solutions was determined by a difference method. The chlorine concentration was determined by the standard FAS titration method. The sum of chlorine plus chloride was determined by reducing the chlorine to chloride with excess hydrazine and measuring the resulting chloride concentration by ion chromatography.

Sampling of gas-phase chlorine. Gas-phase sampling was conducted by drawing air through glass tubes packed with the sulfonamide-functionalized silica gel. The sampling tubes were 6 cm long pieces of 4.5 mm id glass tubing. To prepare the sampling tubes, 0.02 g of gel, supported by a foam plug held in place by a wire clip, was added to the tube, followed by a small piece of glass-wool and an additional 0.05 g of the gel. The 0.02 g of gel was used to evaluate chlorine breakthrough from the 0.05 g portion of gel (see Results and discussion). Each tube was uniquely marked, flow calibrated with a soap-bubble flow meter, and sealed with plastic end-caps until use.

The sample pump used was a battery-powered diaphragm pump (SKC Model 224-PCXR7, Eighty Four, PA, USA). Flow rates ranged from 31 to 294 ml min^{-1} and sampling times ranged from 1 to 4 h. After sampling, tubes were resealed with plastic end-caps until analysis.

Samples were collected at the Buchanan Natatorium at the UNLV campus over two separate periods: January 4–25, 1995, and July 18–August 10, 1995. The sampling site was located ~ 1 m from the edge of the pool at a height of ~ 1 m above the pool. A total of 11 samples were collected in the first sampling period and 21 samples in the second sampling period. Of the 21 collected samples in the second sampling period, four were non-detects and several others were side-by-side samples used to determine method reproducibility (see Results and discussion).

Determination of collected chlorine. A modification of the DPD-based colorimetric method[21] was used for quantification of the collected chlorine. Sampled sorbent was added to a 5 ml calibrated flask, along with 1 ml of phosphate buffer (24 g of Na_2HPO_4, 46 g of KH_2PO_4 and 0.8 g of Na_2EDTA in 1 l), 1 ml of EDTA solution (40 g of Na_2EDTA in 1 l), 1 ml of DPD solution (1.1 g of DPD sulfate, 2 ml of H_2SO_4 and 0.2 g of Na_2EDTA in 1 l) and water to volume. Blanks were made in the same way, except that the sampled gel was replaced with 0.05 g of unsampled gel. Standard solutions were made in the same manner as the blanks, except that appropriate aliquots of a stock standard chlorine solution were also added to the flask.

Absorbances were read *versus* a water reference at 515 nm on either a Varian (Palo Alto, CA, USA) DMS-300 spectrophotometer or a Bausch and Lomb (Rochester, NY, USA) Spectronic 20 spectrophotometer. Blank absorbance values were subtracted from sample and standard absorbances before analyzing the data.

Results and discussion

Characterization of sulfonamide sorbent

Chlorine capacity. Qualitative characterization of the sulfonamide-derivatized gel demonstrated a considerably greater capacity for chlorine than underivatized silica gel; furthermore, the *N*-chlorinated version of the derivatized gel retained an ability to oxidize other substances (*e.g.*, N_2H_4 to N_2) that is characteristic of *N*-chloro-*N*-alkylsulfonamides.[15] The chlorination reaction is

$$\vdash\!\!\rangle\mathrm{Si}-\mathrm{CH_2CH_2CH_2NHSO_2CH_3}+\mathrm{Cl_2}\longrightarrow$$
$$\vdash\!\!\rangle\mathrm{Si}-\mathrm{CH_2CH_2CH_2NClSO_2CH_3}+\mathrm{HCl} \qquad (3)$$

Quantitative determination of the chlorine capacity of the sulfonamide-functionalized silica gel, however, gave different results when a direct method (*i.e.*, measurement of active chlorine bound to the gel) was used compared with an indirect method (*i.e.*, measurement of chlorine removed from a standard solution containing a molar excess of chlorine). The data in Table 1 show that part of the active chlorine that is not immobilized in the form of the *N*-chlorosulfonamide is reduced to Cl^- ion. From eqn. (2) and the data for sample 1 (Table 1), the expected active chlorine content in the supernatant liquid is $1.60 - 2(0.514) = 0.57$ mg, or 0.46 mg (29% of the starting amount of chlorine) more than actually observed. Repeating these experiments with underivatized silica gel showed that chlorine was consumed at the rate of 1.7 mg g^{-1} with essentially no active chlorine present on the gel (after washing in the manner described in the Experimental section). However, when the solution concentrations of chlorine were increased, the chlorine removal per gram also increased. These results are consistent with observations of the modified DPD-based spectrophotometric method for collected chlorine (see below).

Investigation of possible causes of chlorine reduction. Several possibilities were investigated to account for the observed chlorine loss. In one experiment, a solution-phase analog of the sulfonamide-based collector, 1,3-di(methanesulfonamido)propane, was synthesized and subjected to repeated chlorination (with aqueous hypochlorite solution) and dechlorination (with aqueous $NaHSO_3$). NMR studies of the compound before and after the chlorination–dechlorination sequence revealed no chlorination of the alkyl or aryl side-chains, suggesting that this mechanism for chlorine reduction is unlikely.[22] However, series of alkylated silicas (methyl, octyl and octadecyl) were synthesized and tested for chlorine uptake (with aqueous hypochlorite solution, as detailed above). Loss of chlorine was observed on these derivatized silicas that was intermediate in magnitude between untreated silica and the sulfonamide-derivatized sorbent.[23]

Washing of all derivatized silicas was carefully performed to minimize the possibility that unreacted materials would produce unwanted side-reactions. The silica itself was treated in various ways, including acid washing, base washing and repeated chlorination–dechlorination, without noticeable effect on its reactivity. However, using a different attachment chemistry that forms a surface coating rather than bonding directly to the surface, it is possible routinely to obtain quantitative recoveries of chlorine from sulfonamide-based sorbents.[24] Because silica is a highly heteroenergetic surface, entering into, *e.g.*, complexation[25] and adsorption[26] reactions with a number of small polar molecules, and because derivatization of silica surfaces with silanes always leaves unreacted silanol groups,[27] this apparent reaction between chlorine and silica is not a surprising observation.

Table 1 Results of a chlorine capacity experiment

	Sample 1	Sample 2
Before reaction with gel—		
Total Cl^- (aq.) + Cl_2 (aq.)/mg	2.51 ± 0.12	2.51 ± 0.12
Cl_2 (aq.)/mg	1.60 ± 0.02	1.58 ± 0.02
After reaction with gel—		
Total Cl^- (aq.) + Cl_2 (aq.)/mg	2.20 ± 0.11	2.20 ± 0.11
Cl_2 (aq.)/mg	0.112 ± 0.008	0.020 ± 0.008
Cl_2 (gel)/mg	0.514 ± 0.025	0.576 ± 0.025
Mass of gel/g	0.1050	0.1139
Chlorine capacity/mg g^{-1}	9.8 ± 0.6	10.2 ± 0.6
'Excess' reduction of Cl_2 to Cl^- (%)	29	26

Determination of collected chlorine. Despite the fact that some excess reduction of chlorine to chloride occurs in the presence of the sulfonamide-based sorbents, the effect is reproducible, which makes quantification of surface-bound chlorine possible. Experiments conducted with chlorine-spiked sorbent samples demonstrated that when these samples were combined with the DPD colorimetric reagents (described in the Experimental section), the measured solution absorbance was 30–40% less than that of a solution prepared in the same manner with the same chlorine concentration but in the absence of the sorbent. The percentage lowering of the absorbance was observed to be constant across the concentration range typically used for calibration curves, so the addition of 0.05 g of sorbent to each standard and blank solution was incorporated into the standard procedure. Fig. 1 shows a typical calibration curve, and demonstrates that response to active chlorine is linear and uniform within a given batch of sorbent.

Sampling of gas-phase chlorine. Breakthrough was negligible during sampling experiments. In early experiments, the first and second sorbent segments were both 0.05 g, but after initial results showed the breakthrough to be negligible, the size of the second sorbent segment was reduced to 0.02 g. A typical absorbance value for the blank was 0.02; very few of the second sorbent sections in sampled tubes gave absorbances significantly above this level. If 0.01 absorbance units is considered as the uncertainty in this measurement, and if this is compared with a typical sample (*i.e.*, first sorbent section) absorbance of 0.10, a minimum conservative estimate of collection efficiency is 90% (see also Results section).

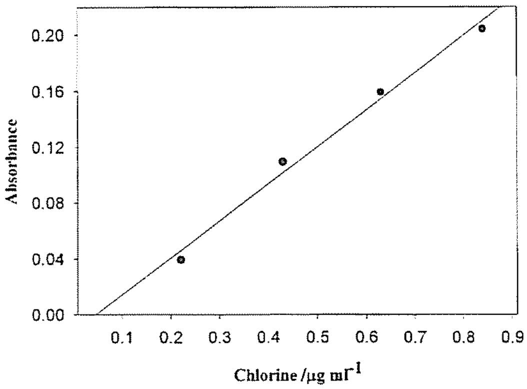

Fig. 1 Calibration curve for chlorine determination by modified DPD colorimetric method. Linear regression gives $y = 0.265x - 0.010$ ($r^2 = 0.995$).

Results. Table 2 gives a summary of measured air concentrations of chlorine at the Buchanan Natatorium on the UNLV campus. It should be noted that the chlorine values measured in the July–August period are more typical than the January measurements; part of the reason for the difference was the higher aqueous chlorine concentration in January (3.9, 3.9 and 4.0 μg ml^{-1} for the January dates; 2.7 μg ml^{-1} for early August). Using expected pH and chlorine concentration ranges for swimming pools, and standard literature values for the K_a of HOCl, K_H for HOCl and K_{eq} for the aqueous Cl_2–HOCl equilibrium,[28] one obtains air concentrations of 0.010–0.100 ppmv for HOCl, in good agreement with the July–August data. Factoring in the chloramine equilibria would considerably complicate the calculations, because the K_Hs for the chloramines are orders of magnitude greater (*i.e.*, more soluble) than HOCl,[29] but the fraction of active chlorine in the form of chloramines is dependent on the ammonia concentration.

In Table 2, the January data represent consecutive samples taken on the date indicated. Samples 16–20 in the July–August sampling period were side-by-side duplicates taken to determine method reproducibility. Samples 21–26 were taken in pairs with overlapping but different sample times to confirm linearity of chlorine collection. Concentrations marked with an asterisk indicate that the sample absorbance was less than the lowest standard, and that the uncertainty in the measured concentration is therefore relatively high.

Analytical results are reported as Cl_2 concentrations, but in fact with this method, the reported concentration represents the sum of active chlorine species. In aqueous solution, Cl_2, HOCl, NH_2Cl, $NHCl_2$, and NCl_3 are known to be collected quantitatively by sulfonamide-based resins,[18] and laboratory experiments with surface coated sulfonamide sorbents[24] have confirmed that Cl_2 gas can be collected quantitatively down to sub-ppbv levels.[30] It would be very surprising if HOCl were not collected quantitatively and surprising if the chloramines and dichlorine monoxide (Cl_2O) were not also quantitatively collected. However, the affinity of sulfonamide substrates for chlorine dioxide (ClO_2) is expected to be low,[31] while the affinity for exotic species such as nitrosyl chloride (NOCl) is unknown. Further characterization work continues in our laboratory.

Table 2 Chlorine concentrations in air at the Buchanan Natatorium, UNLV

Sample No.	Date	Volume sampled/l	Air concentration (ppmv)[a]
1	1/4/95	5.56	0.27
2	1/4/95	5.10	0.30
3	1/4/95	3.88	0.31
4	1/18/95	6.67	0.19
5	1/18/95	5.80	0.24
6	1/18/95	5.46	0.29
7	1/18/95	5.62	0.26
8	1/25/95	5.54	0.17
9	1/25/95	5.62	0.19
10	1/25/95	5.72	0.19
11	1/25/95	5.46	0.21
12	7/18/95	11.1	0.096
13	7/19/95	13.6	0.062
14	7/20/95	17.6	0.053
15	7/21/95	18.0	0.080
16a	7/25/95	18.5	0.075
16b	7/25/95	19.5	0.061
17a	7/26/95	21.0	0.025
17b	7/26/95	22.6	0.023
18a	8/1/95	35.2	0.005[b]
18b	8/1/95	34.5	0.006[b]
19a,b	8/2/95	55.3	ND
20a,b	8/3/95	42.9	ND
21	8/8/95	5.54	0.016[b]
22	8/8/95	28.0	0.008[b]
23	8/9/95	19.1	0.014[b]
24	8/9/95	6.30	0.020[b]
25	8/10/95	30.0	0.005[b]
26	8/10/95	36.0	0.008

[a] The ppmv mixing ratios were calculated from μg m^{-3} values by applying the ideal gas law. The propagated uncertainty for most values is about ±10%. [b] These measurements had absorbance values less than the lowest standard and therefore have uncertainties of ≥20%.

Interferences. This method should be relatively free of interferences. A high ratio of HNO_2 to active chlorine could conceivably consume all the reaction sites and cause a negative error (see Chemistry of sulfonamides section), but nitrous acid is seldom present at high concentrations in most air samples.

The presence of oxidants other than the immobilized *N*-chlorosulfonamide would cause a positive error in the DPD-based colorimetric determination. Ozone, H_2O_2 and organic peroxides are often present in ambient air and could be considered as potential interferents. However, for that event to occur, the interferents would have to be of concentration comparable to that of the active chlorine and they would have to be adsorbed on the surface, since they do not form an oxidizing species when reacted with a sulfonamide. Therefore, the interferents could in principle be removed by rinsing the substrate with distilled water before the colorimetric determination.

For the application shown here (*i.e.*, total active chlorine concentration over a swimming pool), the peroxide levels are completely negligible compared with the chlorine concentration, and the ozone concentration is very unlikely to be significant in comparison with the chlorine concentration. The presence of non-detects in the data set would also argue against an ozone interference in the current application.

Conclusions

The use of a sulfonamide sorbent for collection of atmospheric chlorine has been shown to be feasible. The sorbent material is easy to prepare and has a high affinity for aqueous and airborne combined active chlorine. Collected chlorine retains its oxidizing power, and this property can be used to determine the amount of detected chlorine. Although not pursued here, other studies have shown that bromine reacts with sulfonamide resins in a similar manner to chlorine,[16] so that the method could be extended to bromine determination. The method would not be able to distinguish bromine from chlorine, however. Few interferences are expected owing to the high selectivity of the chemistry, but further characterization (*e.g.*, under extreme conditions) of potential interferents could be pursued. Further work is under way to characterize related collection materials (*e.g.*, new compounds and substrates) and to extend the detectable concentrations to lower values using different analytical detection methods.

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References

1 G. C. White, *Handbook of Chlorination and Alternative Disinfectants*, Wiley, New York, 4th edn., 1999.

2 Assembly of Life Sciences (US), Committee on Medical and Biologic Effects of Environmental Pollutants, *Chlorine and Hydrogen Chloride*, National Academy of Sciences, Washington, DC, 1976.

3 A. A. P. Pszenny, W. C. Keene, D. J. Jacob, S. Fan, J. R. Maben, M. P. Zetwo, M. Springer-Young and J. N. Galloway, *Geophys. Res. Lett.*, 1993, **20**, 699.

4 W. C. Keene, A. A. P. Pszenny, D. J. Jacob, R. A. Duce, J. N. Galloway, J. J. Schultz-Tokos, H. Sievering and J. F. Boatman, *Global Biogeochem. Cycles*, 1990, **4**, 407.

5 H. B. Singh and J. F. Kasting, *J. Atmos. Chem.*, 1988, **7**, 261.

6 M. E. Cassinelli, *Appl. Occup. Environ. Hyg.*, 1991, **6**, 215.

7 US OSHA, Analytical Laboratory, *OSHA Analytical Methods Manual*, USDOL/OSHA Method No. ID-101, American Conference of Governmental Industrial Hygienists, Cincinnati, OH, 1985.

8 A. Jain and K. K. Verma, *Chromatographia*, 1993, **37**, 492.

9 R. J. Rando and H. G. Poovey, *Appl. Occup. Environ. Hyg.*, 1993, **8**, 126.

10 N. Takenaka, S. Itoh, M. Kitano, Y. Maeda and M. Munemori, *Anal. Chim. Acta*, 1992, **266**, 353.

11 C. W. Spicer, E. G. Chapman, B. J. Finlayson-Pitts, R. A. Plastridge, J. M. Hubbe, J. D. Fast and C. M. Berkowitz, *Nature* (*London*), 1998, **394**, 353.

12 J. R. Maben, W. C. Keene, J. N. Galloway and A. A. P. Pszenny, poster presented at the American Geophysical Union Fall Meeting, December 6, 1993, Poster A12B-10.

13 W. C. Keene, J. R. Maben, A. A. P. Pszenny and J. N. Galloway, *Environ. Sci. Technol.*, 1993, **27**, 866.

14 D. W. Emerson, D. T. Shea and E. M. Sorenson, *Ind. Eng. Chem. Prod. Res. Dev.*, 1978, **17**, 269, and references cited therein.

15 D. W. Emerson, D. Gaj, C. Grigorian and J. E. Turek, *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.*, 1982, **23**, 289.

16 D. W. Emerson, *Ind. Eng. Chem. Res.*, 1988, **27**, 1797.

17 D. W. Emerson, *Ind. Eng. Chem. Res.*, 1990, **29**, 448.

18 D. W. Emerson, *Ind. Eng. Chem. Res.*, 1991, **30**, 2426.

19 D. W. Emerson, *Ind. Eng. Chem. Res.*, 1993, **32**, 1228.

20 B. J. Johnson, S. C. Huang, A. Wong and L. Yao, *Microchem. J.*, 1994, **49**, 78.

21 American Public Health Association, American Water Works Association and Water Pollution Control Federation, *Standard Methods for Examination of Water and Wastewater*, American Public Health Association, Washington, DC, 16th edn., 1985, pp. 306–310.

22 B. Tadepalli, Master's Thesis, University of Nevada, Las Vegas, NV, 1995, pp. 32–36.

23 J. Floyd, D. Emerson and B. Johnson, UNLV Chemistry Department, unpublished data, 1995.

24 L. Song, Master's Thesis, University of Nevada, Reno, NV, 1997, pp. 66–74.

25 C. Chiang and J. L. Koenig, *J. Colloid Interface Sci.*, 1981, **83**, 2.

26 J. M. Lorrain, C. R. Fortune and B. Dellinger, *Anal. Chem.*, 1981, **53**, 1302.

27 A. B. Scholten, J. W. de Haan, H. A. Claessens, L. J. M. van de Ven and C. A. Cramers, *Langmuir*, 1996, **12**, 4741.

28 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Wiley, New York, 1980, 4th edn., pp. 556–558.

29 G. Holzwarth and S. L. Balm, *Water Res.*, 1984, **18**, 1421.

30 A. Ali, K. Adoor, D. Emerson and B. Johnson, UNLV Chemistry Department, unpublished data.

31 D. W. Emerson, *Microchem. J.*, 1994, **50**, 116.

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