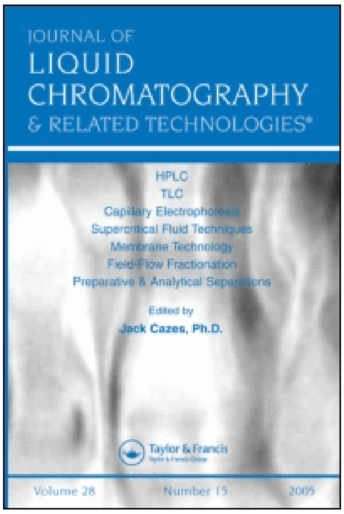

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

Determination of Chlorine and Chlorine Dioxide by Non-Suppressed Ion Chromatography and Application to Exposure Assessment in the Paper Industry

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To cite this Article Poovey, H. G. and Rando, R. J.(1995) 'Determination of Chlorine and Chlorine Dioxide by Non-Suppressed Ion Chromatography and Application to Exposure Assessment in the Paper Industry', Journal of Liquid Chromatography & Related Technologies, 18: 2, 261 — 275

To link to this Article: DOI: 10.1080/10826079508009237

URL: http://dx.doi.org/10.1080/10826079508009237

JOURNAL OF LIQUID CHROMATOGRAPHY, 18(2), 261-275 (1995)

DETERMINATION OF CHLORINE AND CHLORINE DIOXIDE BY NON-SUPPRESSED ION CHROMATOGRAPHY AND APPLICATION TO EXPOSURE ASSESSMENT IN THE PAPER INDUSTRY

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ABSTRACT

A non-suppressed ion chromatography method for the determination of chlorine and chlorine dioxide by their representative ions, chloride and chlorite, has been developed. The method utilizes a phosphate buffered iodide solution for the absorption of chlorine and chlorine dioxide from air and conversion to their representative ions. Analysis is by non-suppressed ion chromatography with a 1-hexane sulfonic acid, sodium salt mobile phase and detection by conductivity. The analytical detection limit was found to be 0.16 μg/mL and 0.13 μg/mL for chloride and chlorite, respectively. The method was adapted for use in a passive sampler and used to assess exposure to chlorine and chlorine dioxide at four pulp / paper mills. A total of 336 personal exposure samples were collected of which 25.2% had detectable levels of chlorine and 3.9% had detectable levels of chlorine dioxide. For those samples with detectable exposures, the overall geometric means and standard deviations were GM = 38 ppb, σ_g = 2.5 and GM = 33 ppb, σ_g = 2.5, for chlorine and chlorine dioxide, respectively.

INTRODUCTION

The ability to simultaneously detect chlorine and chlorine dioxide is of concern in the workplace where there is concomitant exposure. Chlorine and chlorine dioxide are used extensively as bleaching agents in the production of pulp and paper, flour, leather, and textiles. Due to its ability to produce explosive mixtures in air and its chemical instability, chlorine dioxide is generally produced at the site of its use.(1) Both chlorine and chlorine dioxide are strong oxidizers and severe irritants, causing irritation and conjunctivitis at low exposure levels; higher exposure levels or extended exposure times may result in lower respiratory irritation, including pulmonary edema. The current Occupational Safety and Health Administration (OSHA) permissible exposure limits (PEL) for an eight-hour time-weighted-average (TWA) are 0.1 ppm and 1.0 ppm, with short-term exposure limits (STEL) of 0.3 ppm and 1.0 ppm, for chlorine dioxide and chlorine, respectively.(2)

An established method for the collection and quantitation of airborne chlorine and chlorine dioxide utilizes a neutral-buffered phosphate / iodide absorbing solution with spectrophotometric analysis of formed iodine at 350 nm. The sample is analyzed at neutral and acid pH's in order to separately quantitate both Cl_2 and ClO_2:(3)

At Neutral pH:

$$Cl_2 + 2\,I^- \longrightarrow I_2 + 2\,Cl^-$$

$$ClO_2 + I^- \longrightarrow \tfrac{1}{2}\,I_2 + ClO_2^-$$

At Acid pH:

$$ClO_2^- + 4\,H_3O^+ + 4\,I^- \longrightarrow 2\,I_2 + Cl^- + 6\,H_2O$$

It is seen that under neutral pH conditions, the ions, chloride and chlorite, are surrogate analytes for chlorine and chlorine dioxide, respectively. A suppressed ion chromatographic technique was developed which increased the sensitivity, specificity, and simplicity of the neutral-buffered iodide method by simultaneous determination of the representative ions, Cl^- and ClO_2^-, at a single pH.(4-5) The purpose of this work was to adapt this method to a non-suppressed ion chromatography analytical system. The technique was subsequently utilized for exposure assessment of workers in four pulp/paper mills using sample collection by personal passive dosimeter(6-7) containing the neutral-buffered iodide absorbing solution.

MATERIALS AND METHODS

The analytical system consisted of a Waters M-6000A pump and an AllTech/Wescan ICM-300 ion chromatography module which included an oven set at a temperature of 30°C, a 100 μl PEEK sampling loop, and a model 315 conductivity detector set at 5 μS full scale. The output of the conductivity detector was recorded and integrated on a SpectraPhysics Datajet integrator.

Due to its wide range of tolerance to pH (2 to 12) and organic solvent percentage (0-100), the initial screening of mobile phase for chromatographic resolution of chloride and chlorite was done with an Alltech universal anion column, 10 μm particle size with column dimensions of 150 mm x 4.6 mm. Several common ion chromatography mobile phases, including potassium hydrogen phthalate (EM Science), sodium hydroxide (J.T. Baker), sodium bicarbonate (Fisher), and ethylenediaminetetraacetic acid, disodium salt (EDTA), (Aldrich), were screened. The alkanesulphonates, 1-octane sulfonic acid, sodium salt (Aldrich) and 1-hexane sulfonic acid, sodium salt (Aldrich), which have been utilized as ion association agents in HPLC(8) were also screened. All these mobile phases were tested over a range of concentration, pH, and flow rate.

After optimization of mobile phase, analyses were done on a Wescan conventional anion/s column, 10 μm particle size with column dimensions of 250 mm x 4.6 mm. Due to the high affinity of this column for iodide, it was pretreated with 500 mLs of a 1% sodium iodide solution adjusted to a pH of 4.5 with acetic acid.

For collection of air samples, the absorbing medium consisted of 1 mM sodium phosphate - monobasic, 1 mM sodium phosphate - dibasic, and 10 mM sodium iodide. This solution was prepared in the following manner: 2 millimoles sodium phosphate, dibasic, 99.95% (Aldrich), and 2 millimoles sodium phosphate, monobasic, 99% (Aldrich) were diluted to 50.0 mL with distilled, deionized water. An aliquot of this solution was diluted 1:10 with distilled, deionized water and analyzed by ion chromatography to screen for interfering compounds and chloride contamination. To remove the interfering peaks, this solution was filtered through an Alltech Maxi-clean IC-OH cartridge. This procedure was repeated until the solution was clean, usually requiring the use of four cartridges. After this procedure, 25 mls of the cleaned phosphate solution were added to 10 millimoles of sodium iodide, 99.99% (Aldrich), and diluted to one liter with distilled, deionized water. The pH of this solution was adjusted to 8.5 with sodium hydroxide then filtered through an Alltech 0.2 μm, Nylon 66 filter and stored in the refrigerator until use.

All samples and standards were prepared in the absorbing media. Standards were prepared from sodium chloride, 99.999% pure (Aldrich), and sodium chlorite, 80% pure (Aldrich). Initially, the purity of a particular lot of sodium chlorite was determined by the single buffer dual pH 350 nm spectrophotometric method.(3) The amount of chloride in the chlorite was quantitated by ion chromatographic analysis of a stock solution in comparison to a chloride standard curve. In subsequent use, the chlorite content was confirmed by the ratio of the chlorite and chloride peaks in a chlorite stock solution: a reduction in the chlorite to chloride ratio indicated a decomposition of the sodium chlorite reagent.

Solutions of ions screened as potential interferants included acetate, carbonate, nitrate, nitrite, sulfate, and sulfide; all were prepared from their respective sodium salts, and only high purity reagents were used to minimize chloride contamination.

Personal exposure monitoring for chlorine and chlorine dioxide using the optimized non-suppressed ion chromatographic method was conducted at four paper / pulp mills. Samples were collected using a modified Tulane passive sampler.(9) As seen in Figure 1, the modified sampler consisted of a 37 mm polystyrene filter cassette with teflon filters (Millipore FA) chemically welded to the exterior and interior faces using methylene chloride. The liquid sample chamber volume was reduced by the inclusion of eighteen 6 mm borosilicate glass balls. The balls were prewashed with chromic acid and rinsed with distilled deionized water. The exterior of the sampler was painted black to prevent photodegradation of the sample. In use, the sampler was filled with approximately 3 mL of absorbing solution and clipped onto the worker's collar. After the monitoring period (usually a full 8-hour shift), the sampler was retrieved, capped, and stored under refrigeration until analysis. In preparation for analysis, the absorbing solution was extracted from the sampler which was then washed with an aliquot of fresh absorbing medium. The sample and wash were combined and diluted to 4.0 or 5.0 ml with additional absorbing medium.

Due to the ubiquitous presence of chloride ion, caution was required in the preparation of samples to prevent contamination. All containers and approximately 10% of the dosimeters used were washed with absorbing solution and checked by ion chromatography for chloride contamination. In addition about 10% of the passive samplers brought to the field were randomly chosen and held as blanks which were subsequently checked for contamination.

Prior to use in the field, the passive sampler was calibrated in the laboratory using standard test atmospheres of Cl_2 and ClO_2 generated in a bench top exposure system. Chlorine test atmospheres were prepared by dilution of chlorine in nitrogen mixtures from a compressed gas cylinder with room air. Chlorine dioxide test atmospheres were prepared using the NCASI

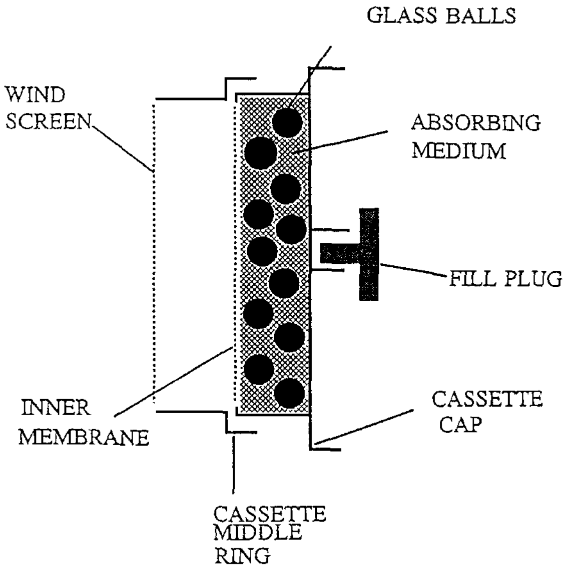

FIGURE 1 Schematic diagram of modified Tulane passive dosimeter.

generator which involves passing a stream of chlorine through a solution of $NaClO_2$, which quantitatively converts chlorine to chlorine dioxide.(10) The sampler was calibrated over a range of exposure concentrations and exposure times. The primary calibration was performed at 25°C; supplemental correction factors were developed at temperatures of 15°C and 35°C.

RESULTS AND DISCUSSION

Mobile phases prepared from sodium hydroxide, sodium bicarbonate, and EDTA all showed high background conductance and excessive system noise. Separation of chloride and chlorite was achieved with a potassium hydrogen phthalate mobile phase, but an inability to resolve the indicating ions from other ions in the absorbing media limited its usefulness as a mobile phase. Separation was not achieved with 1-octane sulfonic acid. A 3.5 mM 1-hexane sulfonic acid, sodium salt mobile phase, adjusted to pH 4.4 with acetic acid, and pumped at a flow of 2.0 mLpm, achieved separation of the indicating ions, chloride and chlorite, from each other and from possible interfering peaks in the absorbing solution. A chromatogram of a standard solution of Cl^- and ClO_2^-, obtained with the optimized chromatographic conditions, is shown in Figure 2.

Different lot numbers of the column resulted in slight alterations of retention times of the ions but was correctable by adjusting the pH of the mobile phase over a range of 4.1- 4.7. Column ageing also required adjustment of the mobile phase pH to maintain separation of the ions.

To prevent microbial growth, the column was stored in a 50% acetonitrile / 50% water solution when not in use. All solutions, including the mobile phase, were susceptible as well and were filtered through a 0.2 μm filter and stored in the refrigerator when not in use to reduce the risk of microbial contamination and growth.

Peaks from unknown contaminants in the phosphates and sodium iodide used to make the absorbing solution required the testing of several batches of these chemicals of different purities from a variety of suppliers. The use of very high purity reagents was required to eliminate these unknown peaks. However, even with high purity reagents, the phosphates required further clean up with an anion exchange resin before the addition of the iodide.

Several ions were screened as possible interferences. The representative ions for carbon dioxide (carbonate) and nitrogen dioxide (nitrate and nitrite) were selected due to their relatively ubiquitous presence in air. Sulfate and sulfide were selected due to the presence of sulfur compounds in the paper industry environment. Acetate was considered due to its use in adjusting the pH of the mobile phase used in the analysis of the samples. Because airborne bromine would be absorbed by the sampling media, the possible interference of bromide ion was also examined. Of the ions screened,

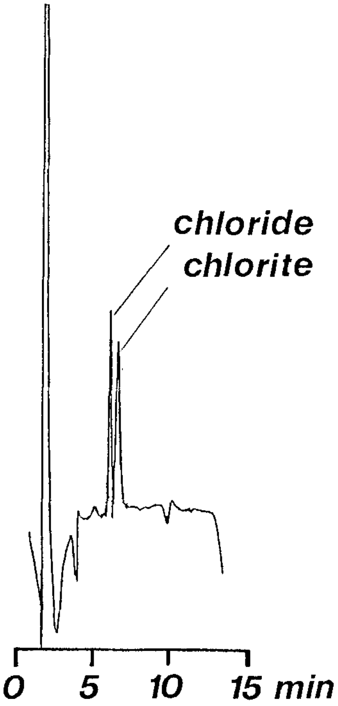

FIGURE 2 Chromatogram of mixed standard of chloride and chlorite, both 10 μg/ml. IC conditions: 250 mm x 4.6 mm Wescan conventional anion/s column; 3.5 mM 1-hexane sulfonic acid sodium salt, adjusted to pH 4.5 with acetic acid and pumped at 2.0 mLpm. Detection: conductivity at 5 μS full scale.

only nitrate had a retention time within one minute of either of the representative ions, eluting 0.7 minutes after the chlorite. Nitrite had the next closest retention time eluting almost two minutes after the chlorite. Bromide, sulfide and acetate all had retention times less than three minutes; where as sulfate and carbonate had significantly longer retention times than chloride or chlorite. The results of these screenings show that none of the ions considered would normally interfere with the chromatographic analysis of chloride and chlorite.

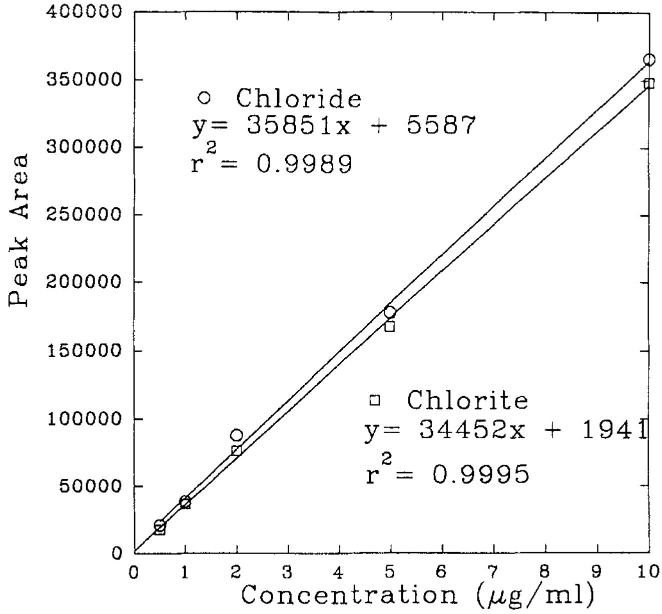

FIGURE 3 Standard curves for ion chromatographic analysis of chloride and chlorite.

Since chlorite ion is unstable in light and thermally degrades with time, standards and samples should be stored in opaque containers in the refrigerator. In general, samples should not be stored for more than two weeks and fresh standards should be made on a weekly basis.

A representative standard curve can be seen in Figure 3. Multiple injections of a 0.5 μg/mL standard resulted in coefficients of variation of 10.5 and 8.8 % for the analytical response of chloride and chlorite, respectively. Based on these results, analytical limits of detection for chloride and chlorite are estimated to be 0.16 μg/mL and 0.13 μg/mL, respectively. This would correspond to air concentrations of 19 ppb chlorine and 16 ppb chlorine dioxide in a 30 liter sample actively collected in 10 ml of absorbing media. Likewise, for the 37-mm modified Tulane passive sampler with a *final*

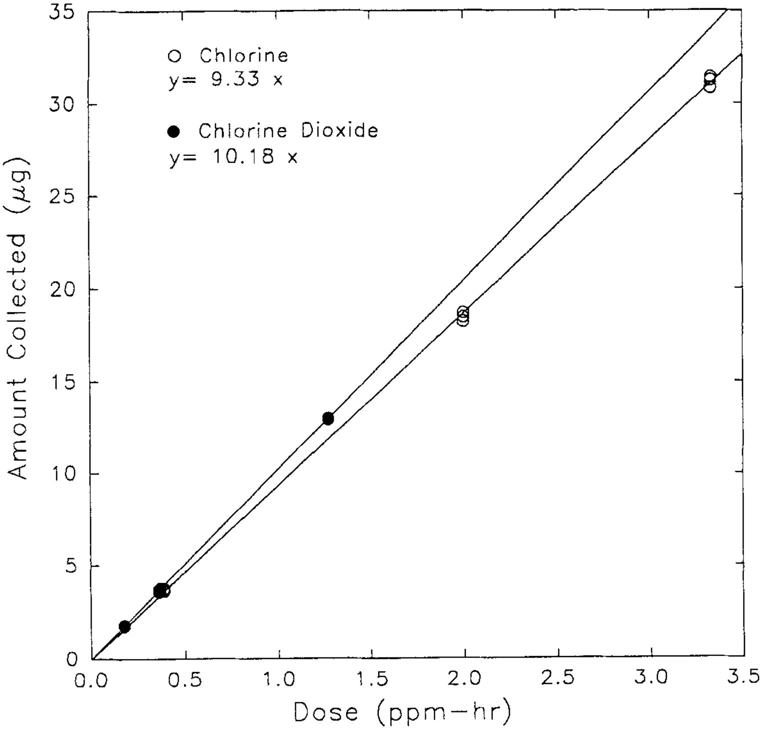

FIGURE 4 Calibration of passive sampler for chlorine and chlorine dioxide at 25°C and 43% RH.

absorbing media volume of 5.0 ml and 8 hours of exposure, the method detection limits would be approximately 10 ppb for both chlorine and chlorine dioxide.

Calibration of the modified Tulane passive sampler yielded mass transfer constants of 9.33 μg/ppm-hr and 10.18 μg/ppm-hr for chlorine and chlorine dioxide at 25°C as seen in Figure 4. Slight temperature corrections were necessary for use under conditions warmer or cooler than 25°C as seen in Figure 5.

The passive sampler was used to assess exposure to chlorine and chlorine dioxide at four paper / pulp mills, see Figure 6 for sample

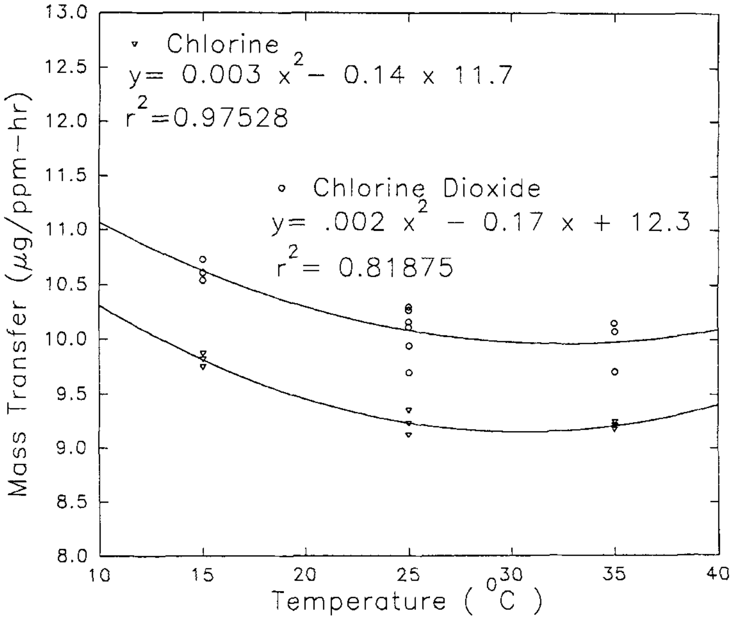

FIGURE 5 Effect of temperature on mass transfer rate of modified Tulane passive sampler for chlorine and chlorine dioxide.

chromatogram. These four mills have undergone conversion to the chlorine / chlorine dioxide bleaching process within the last five years. At the same time, modifications were made to process equipment and procedures to reduce the emission of the chlorine gases and thus the potential for exposure of the workers. At each of the four mills, a total of nine work shifts were monitored over a period of 5 work days. On each shift, approximately 10 workers from various areas of the plant were monitored for exposure. This resulted in a total of 336 personal exposure samples being collected at the mills. Of these, 85 (25.2%) had detectable levels of chlorine and only 13 (3.9%) showed any chlorine dioxide. For those samples with detectable exposures, the overall geometric means and standard deviations were GM = 38 ppb, $\sigma_g = 2.5$ and GM = 33 ppb, $\sigma_g = 2.5$, for chlorine and chlorine dioxide, respectively.

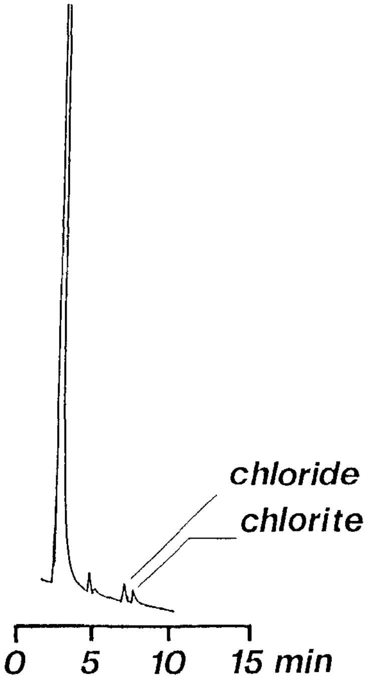

FIGURE 6 Chromatogram of sample from pulp / paper mill. IC conditions as in Figure 2.

A more detailed breakdown of the results of the exposure survey by workareas in the mills is shown in Table 1. In general, exposure to chlorine and especially chlorine dioxide occurs most frequently in the bleach plant areas of these mills. Operators and product testers in these areas may be exposed when entering the bleach washer and generator areas and when collecting samples for quality control. Inadequate ventilation in the bleach plant control room may also result in continuing low-level exposure. Maintenance personnel working on bleach plant equipment also may have frequent exposure to relatively high levels of chlorine and chlorine dioxide. Process upsets and fluctuations may allow residual chlorine and chlorine dioxide to be carried over with the bleached pulp resulting in low-level emissions in the paper

Table 1

Summary Breakdown of Personal Sample Results for Chlorine and Chlorine Dioxide in Four Pulp / Paper Mills*

Work Area	Mill No.	n	Cl_2			ClO_2		
			GM	σ_g	% > LOD	GM	σ_g	% > LOD
woodyard	25	8	18.2	2.6	88	---	---	0
	27	6	7.3	2.6	17	---	---	0
	30	6	10.0	2.8	50	---	---	0
	32	6	---	---	0	---	---	0
pulping		18	13.3	3.2	50	---	---	0
		6	---	---	0	---	---	0
		8	8.3	2.9	25	---	---	0
		4	---	---	0	---	---	0
bleaching		35	11.0	2.8	46	5.7	1.5	14
		42	7.0	2.4	14	5.4	1.7	2.3
		47	6.6	1.8	19	5.4	1.4	6.4
		39	11.9	4.2	28	6.1	2.1	7.7
maintenance		10	10.3	2.3	50	5.8	1.6	10
		24	---	---	0	---	---	0
		11	5.6	1.4	9.1	---	---	0
		7	---	---	0	---	---	0
power plant & chemical recovery		7	26.9	4.4	71	---	---	0
		6	7.4	2.0	33	---	---	0
		3	---	---	0	---	---	0
		9	7.4	3.2	11	---	---	0
paper machines & finishing		10	11.2	2.5	50	---	------	0
		6	---	---	0	---	---	0
		11	6.8	2.1	18	---	---	0
		7	---	---	0	---		0

* GM = geometric mean (ppb), σ_g = geometric standard deviation, % > LOD = percentage of samples with levels of chlorine or chlorine dioxide greater than the limit of detection (~ 10 ppb for either chlorine or chlorine dioxide). For calculation of geometric mean and standard deviation, samples less than the LOD were given a value of ½ the LOD.

machine and finishing areas. Chlorine may also be used in the power plant and boiler houses for water treatment and biocontrol. Other areas of the mill are subject to episodic exposures due to their proximity to the bleach areas and the dispersion of any offgassed chlorine and chlorine dioxide.

CONCLUSIONS

This method provides for simple, specific, and sensitive determinations of chlorine and chlorine dioxide with analysis by their representative ions, chloride and chlorite. The analytical limit of detection was found to be 0.16 μg/ml chloride and 0.13 μg/ml chlorite. Several possible interferants were considered and found not to affect the analysis. This was confirmed with a field test of the method utilizing passive dosimetry at paper mills.

It is recommended that only very high purity reagents be used in the preparation of solutions and that all solutions be filtered and stored in the refrigerator to reduce microbial growth. Care must be taken to prevent contamination of the solutions with chloride from external sources.

Calibration of the modified Tulane passive sampler yielded mass transfer constants of 9.33 μg/ppm-hr and 10.18 μg/ppm-hr for chlorine and chlorine dioxide at 25°C; however, a correction is required to adjust for temperature effects on the mass transfer rate.

Exposure assessment at four paper / pulp mills showed the utility of the method with the geometric mean of the exposures being approximately 1/25 and 1/3 of the PELs for chlorine and chlorine dioxide respectively.

ACKNOWLEDGEMENTS

The authors are grateful to Fred Esmundo, Rachele Gibson, and Byron Lockhart for their technical assistance. This work was supported by a grant from the National Institute of Environmental Health Science, P42ES05946.

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Received: June 24, 1994
Accepted: July 26, 1994