

Note

Determination of chlorine and chlorine dioxide in workplace air by impinger collection and ion-chromatographic analysis

EVA BJÖRKHOLM*, ANNIKA HULTMAN and JAN RUDLING

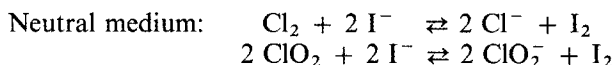
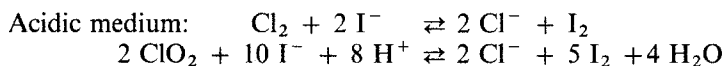
National Institute of Occupational Health, 171 84 Solna (Sweden)

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Chlorine and chlorine dioxide (ClO₂) can be encountered as individual compounds or as mixtures in many working environments such as pulp and textile bleaching and water disinfection. Both gases are known irritants to respiratory organs in very low concentrations. The standard for occupational exposure in Sweden is 0.5 ppm for Cl₂ and 0.1 ppm for ClO₂ as a time-weighted average (8 h). The short-term exposure limit (15 min) is 1.0 ppm for Cl₂ and 0.3 ppm for ClO₂. These values correspond well with standards used in European countries and in the U.S.A.

Most methods for determining Cl₂ and ClO₂ in workplace air are based on absorption in an impinger containing some form of redox indicator, followed by spectrophotometric analysis¹⁻³. The estimation of low levels of both chlorine and chlorine dioxide requires two different absorption solutions⁴, but since Cl₂ and ClO₂ contribute to the colour change in both of the reagent solutions, the absorption values must be corrected yielding lower accuracy. The chlorine that interferes with the analysis of ClO₂ can be removed by sulphaminic acid and sodium hydroxide¹.

One method employs the different reactions of chlorine and chlorine dioxide with potassium iodide in acidic and neutral media respectively⁵. The reactions are as follows:



The absorption occurs in a neutrally buffered solution which is then acidified. The iodine liberated by the reaction reacts with N,N-dimethyl-*p*-phenylenediamine, and a coloured complex is formed which is then determined photometrically. This method is non-specific, being interfered with by other substances which oxidize iodide to iodine or reduce iodine to iodide. According to the reactions above, chlorine and chlorine dioxide are reduced in neutral potassium iodide solution to chloride and chlorite (ClO₂⁻) ions respectively. This paper presents the possibility to separate and quantify the ions formed in one chromatographic experiment.

EXPERIMENTAL

Known levels of Cl_2 and ClO_2 were generated by diluting concentrated gas in air in a dynamic system. For Cl_2 , a gas flask containing 1000 ppm of Cl_2 in nitrogen was used. The ClO_2 was generated by passing helium at 1 l/min over a solution of ClO_2 in water at 13°C (prepared according to ref. 6) in a dark glass bottle. Different concentrations of ClO_2 were obtained by varying the concentration of the solution (vapour pressure of ClO_2) and by changing the diffusion path of the gas by varying the volume of the solution in the bottle. The amount of ClO_2 emitted from the bottle was calculated from the difference shown by thiosulphate titrations immediately before and after the generation.

The chlorine and chlorine dioxide gas was passed into a 5-l round bottom flask, and mixed with air (20 l/min). All flows in the system were regulated with thermal mass-flow gauges which controlled magnetic needle valves. The flows were checked with a bubble gauge or rotometer. The gas mixture was passed forward to a glass container with an outlet for sampling. All connections in the gas-generating system were made of poly(tetrafluoroethylene).

Samples were taken with 30-ml midjet impingers, whose 15.0-ml charge of absorption solution consisted of neutrally buffered 10 mM potassium iodide solution (Merck No. 5043). The buffer contained 10^{-3} M potassium dihydrogenphosphate and 10^{-3} M sodium hydrogenphosphate. For sampling, a vacuum pump was used with a flow-rate adjusted to 1 l/min.

To minimize the background from chloride, all glass equipment was soaked carefully with 1 M carbonate solution and rinsed with distilled water prior to sampling and analysis.

The analysis was performed by ion chromatography. Since the absorption solution contains high levels of potassium and sodium ions, these cause interference peaks at the beginning of the chromatogram. To separate ClO_2^- from these ions, and from formate which is a stabilizer added to potassium iodide* a very weak eluent must be used, yielding a long retention time for I^- .

In order to shorten the analysis time, a simple recoupling was made of the ion chromatograph's two systems (Fig. 1). By first passing the sample through a pre-column, I^- was separated from ClO_2^- and Cl^- . The last two ions were passed on to the separation column and after 1 min the valves were switched so that I^- and phosphate ions were diverted to waste with the aid of pump 2. After the completion of the experiment (elution of Cl^-), the pre-column was ready for another injection and the valves switched back to the original position.

The ion-chromatographic analysis apparatus and conditions were as follows: Dionex 14 ion chromatograph with conductivity detector; HP 3388 integrator; columns, 50 mm \times 4 mm anion concentrator, HPIC-AG1 (Dionex), 250 mm \times 4 mm anion separator, HPIC-AS3 (Dionex), 100 mm \times 4 mm anion suppressor, ASC1 (Dionex); flow-rates, 138 ml/h (analytical column, pump 1), 300 ml/h (pump 2);

* Formate occurred in all the five lots investigated (Merck No. 5043), varying from 0.1 to 0.6%. No formate was seen in potassium iodide Suprapur (Merck No. 5044) and sodium iodide (Merck No. 6523).

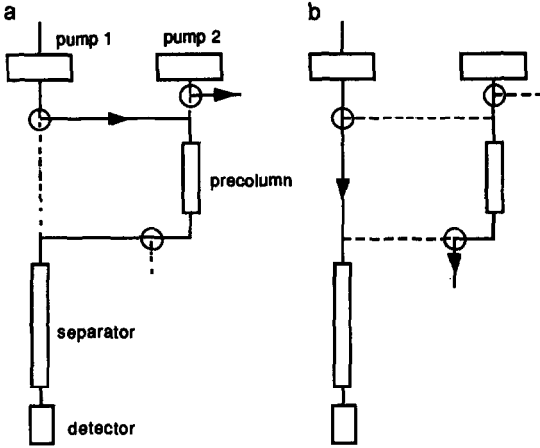


Fig. 1. The two flow systems of the ion chromatograph. (a) Sample passes through the precolumn. (b) Parts of the sample pass through the separation column while the precolumn is cleaned.

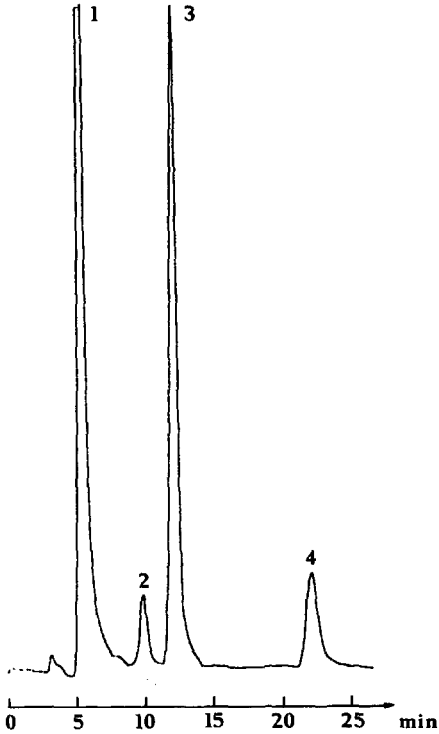


Fig. 2. Chromatogram from analysis of chloride and chlorite ions. Peaks: 1 = sodium and potassium ions; 2 = formate; 3 = 122 μM chlorite; 4 = 24 μM chloride.

injection volume, 100 μ l; eluent, 0.75 mM sodium bicarbonate (both systems); retention times, ClO_2^- ca. 10 min, Cl^- ca. 20 min; measurement region, 3 or 10 μ S.

A typical chromatogram is shown in Fig. 2.

RESULTS AND DISCUSSION

The uptake efficiency of the impinger was determined by sampling with two impingers connected in series. The sampling time varied from 30 to 70 min and the concentrations were 1 ppm of Cl_2 and 0.1–0.3 ppm of ClO_2 . After sampling, the analysis result from the first impinger was compared with the sum from the two impingers. This indicated a collection efficiency of $96 \pm 5\%$ for ClO_2 and $100 \pm 2\%$ for Cl_2 ($n = 6$). Consequently, one impinger can be considered adequate for obtaining a quantitative yield in sampling.

The accuracy and precision were determined for different levels of Cl_2 and ClO_2 with sampling times varying from 30 to 60 min. The results of the chromatographic analyses were compared with the calculated content in the gas-generating system (Table I). The precision of the analysis step was investigated further for ClO_2^- . For a 5 μ M chlorite solution (corresponding to 0.061 ppm at 20°C with a sampling time of 30 min), a coefficient of variation (C.V.) of 1.2% ($n = 5$) was obtained. A concentration of 1.8 μ M ClO_2^- (corresponding to 0.022 ppm under the same conditions) yielded a C.V. of 3.9% ($n = 7$). The calibration graph for ClO_2^- is linear at least within two orders of magnitude. It is thus possible to analyze levels lower than 0.022 ppm, although the C.V. will exceed 3.9%.

The smallest analyzable concentration of Cl^- (twice the chloride background) was about 10 μ M (corresponding to 0.06 ppm Cl_2 at 20°C with a sampling time of 30 min; C.V. = 1.2%, $n = 8$). This rather high level was due to difficulties in fully eliminating the chloride background.

Interfering gases, which may occur in environments where Cl_2 and ClO_2 are encountered, are primarily sulphur dioxide and hydrogen sulphide. These reducing compounds may influence the result for ClO_2 by reacting with ClO_2^- in the solution. Since the reaction between ClO_2 and I^- is very rapid and I^- is present in a vast excess,

TABLE I
ACCURACY AND PRECISION OF THE METHOD

C.V. denotes the coefficient of variation in percent, defined as $100 \cdot \text{standard deviation}/\text{mean value}$ of the content obtained.

<i>n</i>	<i>Generated (ppm)</i>		<i>Obtained (ppm)</i>		<i>Yield (%)</i>		<i>C.V. (%)</i>	
	<i>ClO₂</i>	<i>Cl₂</i>	<i>ClO₂</i>	<i>Cl₂</i>	<i>ClO₂</i>	<i>Cl₂</i>	<i>ClO₂</i>	<i>Cl₂</i>
5	0.41	—	0.42	—	104	—	3.2	—
2	—	1.09	—	1.08	—	99	—	1.4
2	0.38	1.18	0.36	1.24	95	105	2.1	2.3
6	0.10	0.99	0.094	0.91	94	92	4.0	3.5
6		*	1.1	0.8	—	—	4.4	7.3

* Generated concentrations not calculable due to fault in one of the flow gauges.

there is no reason to believe that H_2S or SO_2 interferes with the adsorption process itself. Therefore a simplified test was made. Gases which are representative of current environments (0.14 ppm SO_2 , 2 ppm H_2S) were passed through absorption solutions spiked with ClO_2^- . The sampling time was 30 min and the flow-rate 1 l/min. The concentrations of ClO_2^- in solution corresponded to 0.39 and 0.04 ppm ClO_2 for the SO_2 tests, and 0.20 and 0.02 ppm for the H_2S tests. The analyses were made directly after the sampling, and the stronger chlorite solutions were refrigerated for 2 days and analyzed thereafter. No significant decrease in chlorite contents was registered.

The stability of the solutions during storage was studied by preparing mixtures with known concentrations of Cl^- and ClO_2^- in absorption solution. Each solution was divided into four and placed in separate containers (dark polypropylene bottles) which were completely filled. The four samples were stored thus: (a) 2–5 h at room temperature, (b) 2 days at room temperature, (c) 3 days in a refrigerator and (d) 2 days at room temperature followed by 6 days in a refrigerator. Table II shows that the chlorite concentration decreases during storage at room temperature, but is stable during refrigeration, while the chloride concentration is not affected by storage.

To test the method under more realistic conditions, samples were taken at a pulp bleaching plant. The chlorine dioxide content in the workplace air varied drastically. Besides chlorine and chlorine dioxide, sulphur dioxide and chloroform occurred. The sampling was performed at four fixed sites. At each site, three to five samples were taken simultaneously. The sampling time varied from 110 to 200 min. Two samples were taken consecutively and mixed later. In order to compensate for evaporation, the impingers were weighed before and after sampling. Three of the measuring points were located next to washing filters. One sampling site was chosen near a chlorine dioxide tower on the mixer-level where the pulp is mixed with chemicals. In connection with this test, a serious disturbance of operation occurred, resulting in greatly increased levels of ClO_2 . The precision of the sampling was rather good, the C.V. obtained being less than 6.8%. The results are shown in Table III.

In conclusion, the results reported show that both Cl_2 and ClO_2 in air can be determined simultaneously by ion-chromatographic analysis. As expected, the method is not sensitive to interference. However, the tests reveal that the chlorine dioxide

TABLE II
STORAGE STABILITY

Room denotes storage at 22°C and cold storage at 7°C.

Concentration (μM)		Yield (%) obtained after storage							
ClO_2^-	Cl^-	2–5 h room		2 d room		3 d cold		2 d room + 6 d cold	
		ClO_2^-	Cl^-	ClO_2^-	Cl^-	ClO_2^-	Cl^-	ClO_2^-	Cl^-
2	0	100	—*	104	—	—	—	—	—
2	100	100	100	100	—	—	100	96	100
2	200	100	—	100	—	—	100	100	—
10	100	100	—	88	101	99	100	86	—
10	200	100	—	85	—	96	—	84	—

* Not determined.

TABLE III
FIELD TEST AT A PULP BLEACHING PLANT

Total sampling time was 170–350 min. Coefficient of variation (C.V.) defined as 100 · standard deviation/mean value of content obtained.

Test site	n	Obtained (ppm)		C.V. (%)	
		ClO ₂	Cl ₂	ClO ₂	Cl ₂
At filter A	3	0.11	0.30	4.0	5.6
At filter B	4	0.053	0.090	6.0	6.8
Mixer-level	3	1.67	1.59	2.5	2.6
At filter C	5	0.22	0.12	5.7	3.8

content decreases with storage at room temperature. If analyses cannot be conducted along with the sampling, storage in a refrigerator is recommended. The method makes it possible with a 30-min sampling time to determine levels as low as 0.02 ppm ClO₂ and 0.06 ppm Cl₂ with acceptable precision.

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