

## Quantitative Analysis of Chlorine in Air by Gas Chromatography

A. L. Hunt and J. F. Alder

Department of Instrumentation and Analytical Science, University of Manchester Institute of Science and Technology, P.O. Box 88, Manchester, UK M60 1QD

**A GC method was developed for the separation of gaseous chlorine in air using a dual column switching system eluting to a thermal conductivity detector. The limit of detection was found to be 3 ppm; the linear range up to 300 ppm. Initial separation was achieved with a PoraPLOT Q (25 m  $\times$  0.53 mm id), column with the separation of the permanent gases being achieved with a Molecular sieve 5A PLOT column (25 m  $\times$  0.53 mm id). The resolution of oxygen, nitrogen and carbon dioxide in gaseous samples provides an indication of chromatographic performance.**

Many methods have been employed for the detection of chlorine. Colorimetric methods, such as that used in Draeger tubes are common.<sup>1–4</sup> With Draeger tubes the quantitative measures are subject to error, owing to the lack of precision in reading the distance advanced by the colour change. The colorimetric indicator is *o*-toluidine adsorbed onto silica gel. The limit of detection is dependent on the *o*-toluidine analogue and the  $\lambda_{\text{max}}$  of absorbance. The most sensitive tubes detect chlorine at concentrations as low as 0.001 ppm.<sup>1</sup> As well as colour reactions, the UV absorption of free and combined chlorine may be employed. Molecular chlorine dissolved in carbon tetrachloride has an absorption maximum at 331 nm and a molar absorption coefficient of 95.7 dm<sup>3</sup> mol<sup>–1</sup> cm<sup>–1</sup>. This method, however, is relatively insensitive and is consequently not popular for chlorine determination.<sup>5</sup> Electrochemical methods have been employed for chlorine;<sup>6–9</sup> potentiometric determination is based on interfacial electrochemical potentials and mainly involves measurement of potential differences that exist across membranes that separate the test solutions. The potential difference results from transport of the species through the membrane or the binding of charged species to it and interferences result if selective membranes are not employed. The presence of other chlorine containing compounds can result in erroneous results.

A continuous chlorine analyser was produced commercially,<sup>10</sup> based on the production of iodine from PbI<sub>2</sub> by the chlorine. The iodine was subsequently determined using an iodide electrode.

Only one publication has directly tackled the problem of GC analysis of chlorine.<sup>11</sup> The method was used for the determination of both free chlorine and other chlorine containing organic products such as chlorinated hydrocarbons. Known aliquots of chlorine were mixed with acetone and decane (the internal standard). The resultant monochloroacetone was then analysed by GC–flame ionization detection (FID) or GC–MS. Problems were encountered with this method due to production of the dichloroacetone in varying quantities.

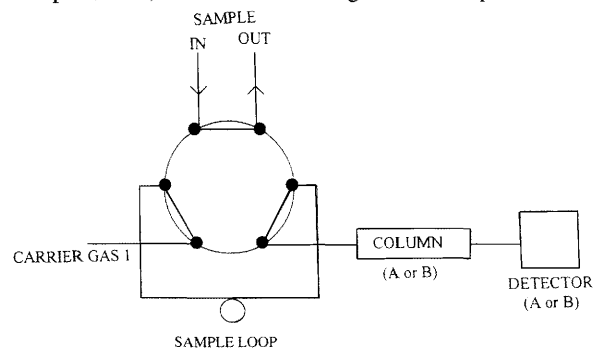
In the present study, a method was developed for the direct determination of chlorine in a gaseous atmosphere comprising mainly air. The aim was to provide a reference method for a chlorine gas blending apparatus used to test chemical sensors,

and then develop a general method for separation and quantification of chlorine and other permanent gases in air.

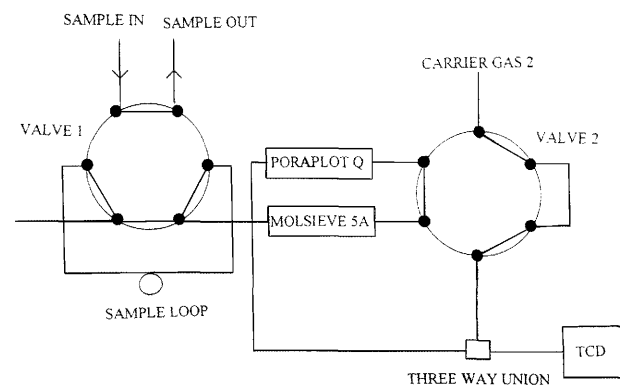
### Experimental

Gas Chromatography was carried out using a Chrompack 9001 gas chromatograph (Chrompack) equipped with a flame ionization detector (Chrompack) and thermal conductivity detector (TCD) (Chrompack). Injection onto each of the two channels was via two six-port valves (Valco) equipped with a 0.25 ml sample loop. The two configurations used are shown in Figs. 1 and 2.

Data acquisition was achieved using a 386DX Opus PC equipped with a SUMMIT (Comus, Kingston-upon-Hull, UK) chromatography control package. All gases were from BOC Special Gases (BOC, London, UK). Helium was used for the carrier and make-up gases. A 1% chlorine in helium mixture was diluted with air in a blending manifold for calibration purposes. Air for the switching valves and FID was cleaned with an RS 724-330 gas regulator and filter system (RS Components, Stockport, UK). All instrument gases were purified using



**Fig. 1** Schematic diagram of single column configuration. Column A, PoraPLOT Q; column B, Molecular sieve 5A; detector A, FID; and, detector B, TCD.



**Fig. 2** Schematic diagram of dual column switching system.



Purichem towers (Chrompack). Gas flows were measured with bobbin rotameters (Platon, London, UK) calibrated against a bubble flow meter. The blending apparatus produced samples in the range 10 000–1 ppm gaseous chlorine in air.

General Procedure

Initial studies were carried out using the configuration in Fig. 1. The usefulness on the single column with each detector was investigated. Conditions for all single column applications are shown in Table 1. Dual column applications and valve switching timed events are shown in Tables 2 and 3, respectively, and the system set-up in Fig. 2.

Results and Discussion

Single Column Studies

PoraPLOT Q

Using the conditions outlined in Table 1, gaseous chlorine and air were satisfactorily separated. The use of the FID was

rejected for further study due to its inability to detect the permanent gases. For chlorine the FID gave good peak shapes with a limit of detection of less than 2 ppm chlorine in air. A linear range was achieved up to approximately 1500 ppm. The results were reproducible with respect to retention time and peak area, but the lower range was reduced with extended column use. Fig. 3 shows the resulting chromatogram. Similar studies were attempted on a similar 10 m PoraPLOT Q (Chrompack) column. While the limit of detection was reduced to less than 1 ppm the retention time was only 12 s and the rise in signal caused by the valve firing tended to interfere with the chlorine peak itself.

The 25 m column was attached to the TCD, resulting in the separation shown in Fig. 4. The retention time was increased due to the much reduced flow rate required to increase detector sensitivity. A limit of detection of 3 ppm was achieved with a linear range up to 300 ppm. The limit of detection was calculated as three times the standard deviation of the baseline noise.

The detectors easily became contaminated with samples containing more than 100 ppm chlorine in air resulting in a 10-fold increase in the limit of detection. This was largely avoided by regularly dismantling the detectors and thoroughly cleaning. When not in use the GC sampled dry clean air and the detectors held at 280 °C.

Table 1 GC operating conditions for single column studies

GC conditions	Molecular sieve 5A		PoraPLOT Q	
	TCD	FID	TCD	FID
Oven temperature limit/°C	180	N/A	280	280
Initial oven temperature/°C	60	N/A	60	60
Final temperature limit/°C	60	N/A	120	60
Temperature rise/°C min <sup>-1</sup>	0	N/A	30	0
Detector temperature/°C	250	N/A	250	250
Injector temperature/°C	100	N/A	100	100
Sampling valve temperature/°C	200	N/A	200	200
Sample volume/cm <sup>3</sup>	0.25	N/A	0.25	0.25
Carrier gas flow/cm <sup>3</sup> min <sup>-1</sup>	17.6	N/A	11.2	13.1
Make-up flow/cm <sup>3</sup> min <sup>-1</sup>	29.15	N/A	8.8	31.2
Air flow/cm <sup>3</sup> min <sup>-1</sup>	N/A	N/A	N/A	255.2
Hydrogen flow/cm <sup>3</sup> min <sup>-1</sup>	N/A	N/A	N/A	33.1

Table 2 GC operating conditions for dual column studies

GC conditions	Level
Oven temperature limit/°C	180
Initial oven temperature/°C	60
Final oven temperature/°C	100
Temperature rise/°C	39.9
Detector temperature/°C	250
Injector temperature/°C	100
Sample valve temperature/°C	200
Sample volume/cm <sup>3</sup>	0.25
*Total flow/cm <sup>3</sup> min <sup>-1</sup>	20.2
*Total flow less make-up/cm <sup>3</sup> min <sup>-1</sup>	11.2

\* These flows relate to the system in by-pass configuration.

Table 3 GC timed events control

Time/min	Description
0.00	Valve 1 to sample
0.00	Valve 2 to series
0.10	Valve 1 to inject
0.10	Start computer integration
0.11	Reset computer integration
1.60	Valve 2 to by-pass
5.00	Stop computer integration
5.01	Reset computer integration

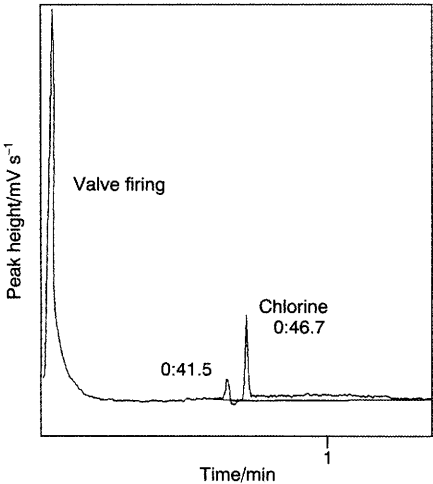


Fig. 3 Separation of chlorine in air on a PoraPLOT Q (25 m × 0.53 id) column (FID).

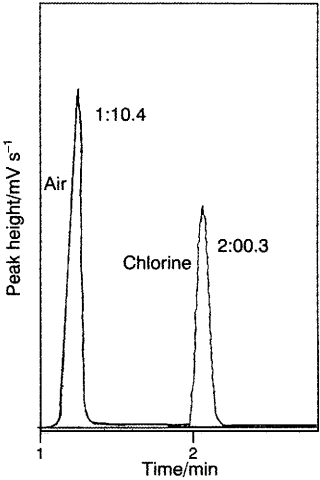


Fig. 4 Separation of 100 ppm chlorine in air on a PoraPLOT Q (25 m × 0.53 id) column (TCD).

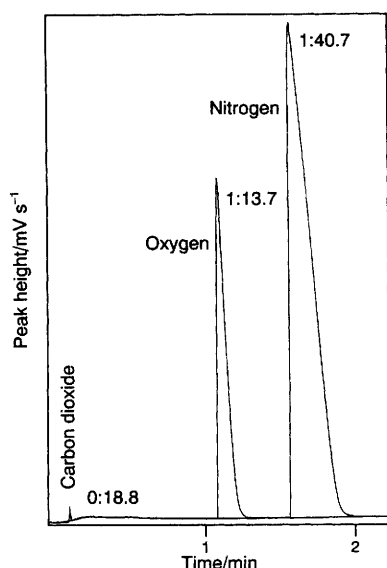
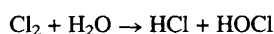


Fig. 5 Separation of air on a Molecular sieve 5A, 25 m PLOT column, 0.531D (TCD).

The single column results led to the development of the system shown in Fig. 2. The installed system was configured to run in a serial by-pass mode with both columns continuing to elute to the TCD. Tables 2 and 3 show the condition and timed events control respectively for the dual column system.

#### Molecular sieve 5A

Fig. 5 shows the separation of the air constituents achieved by the Molecular sieve 5A (Chrompack) column eluting to the TCD. This separation could be implemented by passing the flow eluting from the PoraPLOT Q column to the Molecular sieve 5A for further separation. The molecular sieve column could not be brought into contact with the gaseous chlorine especially in humid air. The heat of the gas sampling valve caused the reaction of chlorine with water as shown in the following reaction scheme:



The products are strongly retained by the Molecular sieve 5A; while this does not harm the column, its presence changes the chromatography and the retention time decreases due to site blocking. Reconditioning of the column restored the original separation. This was achieved by heating the column at 180 °C for 10 h then cooling (10 °C min<sup>-1</sup>) to 100 °C for 5 h.

Drying of the sample before entrance into the GC eliminates the problem, as does separation of chlorine from the test mix prior to the air passing to the molecular sieve. The switching time from serial to by-pass mode was such as to avoid passage of chlorine to the second column.

#### Dual Column Studies

The final system employed (Table 2, Fig. 2) resulted in the separation shown in Fig. 6. Valve 1 is the sampling valve. At the beginning of the analysis, a 0.25 cm<sup>3</sup> sample is injected onto the PoraPLOT Q column which is connected to valve 2, and the carrier gas supply to it controlled by the channel A flow controls. At the start, valve 1 connects the PoraPLOT Q directly to the Molecular sieve 5A. The air constituents and other permanent gases are poorly contained by the PoraPLOT Q and so rapidly pass to the molecular sieve. Valve 2 switches the flow from the first column directly to the TCD via a three-way union,

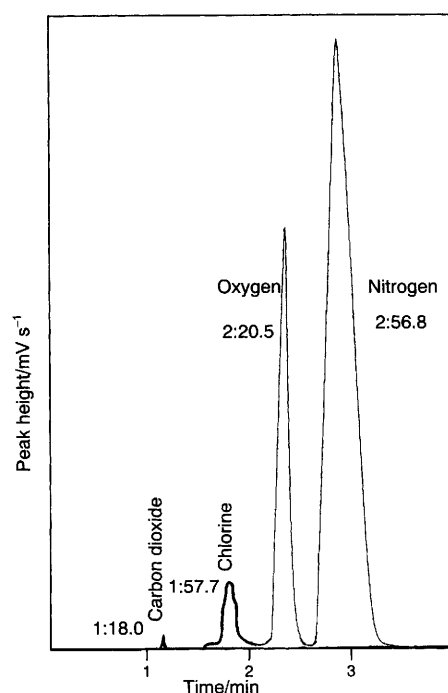


Fig. 6 Separation of 15 ppm chlorine in air using dual column switching system.

at the same time the sampling valve switching the channel flow control to column B. In this way the chlorine passes directly from the PoraPLOT Q column to the detector as does the air, which is now separated into its constituents by the Molecular sieve 5A. The flow rates were carefully controlled to avoid coelution of chlorine and oxygen. The air separation served to act as an internal standard. Since the air constituents in the blending apparatus are standard in each sample, nitrogen will be easily seen if there are any changes in the relative retention times of oxygen. Similarly, a peak area ratio of oxygen:chlorine will help to show any degradation of system sensitivity. A reduction in the excellent reproducibility can be used as an indicator of system degradation. This needed to be carefully monitored due to the highly corrosive effects of chlorine and its hydrolysis products.

The limit of detection of chlorine was unaffected by the use of the Molecular sieve 5A in conjunction with the PoraPLOT Q. The cut time for switching from serial to by-pass mode did affect the limit of detection as well as overall retention times. Careful optimization was required if coelution was to be avoided.

#### Conclusion

The dual column system developed proved to be a reliable way of monitoring chlorine levels in air. The method was reproducible over any 24 h period even at low ppm levels, although the single column studies showed that there was a reduction in the linear range with time. The use of the FID was rejected due to its inability to detect the permanent gases.

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