Journal of Chromatography, 203 (1981) 173–178
Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

CHROM. 13,112

CHLORINE-SELECTIVE DETECTOR FOR LIQUID CHROMATOGRAPHY

STAFFAN FOLESTAD* and BJÖRN JOSEFSSON
Department of Analytical and Marine Chemistry, Chalmers University of Technology, University of Göteborg, S-412 96 Göteborg (Sweden)

SUMMARY

A chlorine-selective detector based on flame emission has been developed for use with high-performance liquid chromatography. The column effluent is first burnt in a hydrogen-rich total consumption burner in the presence of a platinum catalyst. The so-formed hydrogen chloride reacts with indium yielding indium chloride in an upper cool hydrogen flame, thereby emitting a characteristic emission at 360 nm. The detection limit for chloroform in water was 300 pg/sec (signal-to-noise ratio 3:1). The effects of chemical interferences by organic solvents were studied. In the present design, the total column effluent at flow-rates up to 1.5 ml/min is introduced into the detector.

INTRODUCTION

The determination of chlorinated organic compounds is of particular interest in connection with environmental pollution. In this respect, gas chromatography (GC) with halogen-sensitive electron capture has played an important role, and the combination of GC and mass spectrometry has been indispensable for subsequent structure elucidation. Both techniques are mainly limited to the separation of volatile compounds or easily derivatized polar compounds. Non-volatile organic compounds still present problems in analysis. They may be separated in liquid chromatographic systems. However, high-performance liquid chromatography (HPLC) has not yet been successfully combined with a mass spectrometer or chlorine-selective detector.

Specific chlorine determination by neutron activation analysis on environmental samples has shown that the volatile chlorine species comprise only a small proportion of all of the chlorinated constituents[1]. Jolley[2] used ^{36}Cl as a tracer in combination with ion-exchange chromatography in chlorination studies. He identified some non-volatile chlorinated compounds amongst other chlorinated derivatives of nucleic acids.

The need for an elemental chlorine detector in HPLC has led to attempts to use GC detectors such as electron-capture (EC) or photo- and electrolytic conductivity detectors[3–5]. However, the ECD operates in the gas phase which still creates problems with non-volatile components. Conductivity detectors have been used to measure the increased conductivity from hydrogen chloride after pyrolysis or photo-

0021-9673/81/0000–0000/$02.50

degradation of chlorinated compounds[5]. They are not quite selective since other components may yield conducting products.

The direct on-line combination of ion-exchange chromatographic separation and flame photometric detection was successful for selective determination of some metals[6]. Julin *et al.*[7] coupled an HPLC instrument to a modified emission burner to monitor phosphorus- and sulphur-containing compounds. The column effluent was aspirated in an nebulizer with nitrogen and hydrogen gases before entering the burner. Severe quenching was observed when the mobile phase contained organic solvents. Chester[8] inverted the air–hydrogen diffusion flame for selective phosphorus determination. The air burnt in a hydrogen atmosphere thereby changing the redox conditions. In this way the quenching or interference of organic solvents was greatly reduced.

Flame photometric determination of chlorine using the indium chloride emission band at 360 nm was proposed by Gilbert[9]. He used a modified Van der Smissen[10] burner with two air–hydrogen flames. The sample is combusted in the lower burner yielding hydrogen chloride, which in turn reacts with indium before entering the upper flame. In the upper air–hydrogen flame the indium chloride emission band is measured at 360 nm. Gilbert proposed the use of this element selective detector for liquid and solid samples by spraying them into the first air–hydrogen flame, however, no results were presented. Slightly modified versions of this detector have been used successfully in gas chromatographs by several authors[11–14].

Chloride determinations in liquids have been studied by Dagnall *et al.*[15] by using the molecular emission of indium chloride in a cool nitrogen–hydrogen flame. The temperature of the flame was found to exert a strong influence on the formation of the excited indium(I) chloride molecules which results in the intense emission at 360 nm. Belcher *et al.*[16] used molecular emission cavity analysis (MECA) to establish the importance of low temperatures in indium(I) chloride emission.

The combination of a chlorine-selective emission detector, based on the formation of indium(I) chloride, and liquid chromatography would be very attractive in circumstances in which the liquid effluent could be handled in a flame emission detector. By using a total consumption burner to convert the liquid into vapour, combined with a platinum catalyst, the organic chlorine compounds could be efficiently converted into hydrogen chloride for selective chlorine detection.

EXPERIMENTAL

Detector construction and operation

A schematic view of the detector is presented in Fig. 1. It consists of two burners mounted one above the other in a quartz tube chimney. The lower burner is a total consumption burner (Beckman type) combining nebulization and combustion. A continuous flow of column effluent is passed into the turbulent flame from a capillary, and an aerosol is produced in the flame. Large droplets in the flame are not completely converted into vapour and fall down into the drainage. The liquid flow into the burner is in the range 0.5–1.5 ml/min, and those of hydrogen gas (in excess) and air are 4.5 l/min and 1.5 l/min, respectively. The air flow is insufficient to consume all the hydrogen in the lower burner. The excess of hydrogen is used to fuel the upper diffusion burner.

The sample, containing chlorinated organic compounds in water–organic

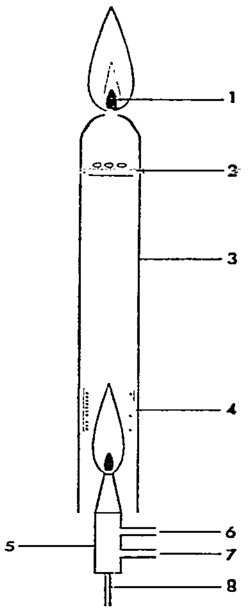


Fig. 1. Schematic view of the detector unit which is mounted on an AAS. 1 = InCl emission reigon; 2 = stainless-steel (SS) net with In, 25 mm below upper flame; 3 = quartz tube (400 × 16 mm I.D.), tube tip 7 mm I.D.; 4 = platinum net, 60 mm above the burner; 5 = total consumption burner (Beckman type); 6 = air inlet; 7 = H_2 inlet; 8 = HPLC column inlet: 0.25 mm I.D. stainless-steel tubing.

Fig. 2. Experimental set-up. To the right is an AAS with the chlorine detector aligned with the entrance optics. To the left is a liquid chromatograph with a UV detector in series with the chlorine detector.

solvent, is combusted in the lower flame. The use of a platinum net as a catalyst in the hydrogen atmosphere makes the conversion into hydrogen chloride more efficient. The hydrogen chloride is then passed over a net of indium (m.p. 156°C) where indium(III) chloride vapour is produced. In the upper cool hydrogen flame a chemiluminiscent reaction (exothermic) occurs. Indium(III) chloride is reduced to excited indium(I) chloride leading to intense emission at 360 nm. The excited indium(I) chloride exists in the cooler part of the flame. The response is dependent on the temperature of the flame which should be kept as low as possible. In the hotter part of the flame the indium(I) chloride is converted into In, InO and In'I. The emission bands of non-chlorine-containing indium species do not interfere with the molecular band at 360 nm. The background emission of the air–hydrogen flame in the absence of chlorine is low, permitting detection of low concentrations of chlorine.

The detector is mounted on a Perkin-Elmer 403 atomic absorption spectrometer (AAS) working in the emission mode (Fig. 2). The position of the chimney and thus the upper flame was adjusted to optimize the indium(I) chloride signal. The slit width was 3 mm, giving a spectral band pass of 2 nm.

To determine the optimal spectrometric conditions for chlorine measurements, *i.e.*, the gas flow, position of indium net, temperature, etc., a continuous flow of water containing 300 ppm chloroform was pumped into the lower burner. The temperature of the indium surface, which should be kept between 250°C and 300°C, was measured with a thermocouple.

Chromatographic system

A LDC liquid chromatographic system with Constametric III pumps and a Gradient Master was used. A Spectra-Physics 770 variable-wavelength UV detector was connected in between the HPLC column and the flame photometric detector. The reversed-phase column employed (200 × 5 mm I.D.) was packed with 5 μm Nucleosil C_{18} (Macherey, Nagel & Co., Düren, G.F.R.). The system was equipped with a Valco injector with 10-μl and 120-μl sample loops and Perkin-Elmer 56 strip-chart recorders.

RESULTS AND DISCUSSION

The detector

The three important aspects of the detector which influence its ability to monitor chlorine species are: (1) the conversion of chlorine compounds into hydrogen chloride in a continuous liquid flow system; (2) the optimal conditions of indium area and temperature, yielding indium(III) chloride; (3) the different reactions in the upper flame which influence the indium(I) chloride emission intensity.

The conversion of organic chlorine compounds in a water flow into hydrogen chloride by means of a total consumption burner using hydrogen as fuel gas is not complete, and the introduction of a platium catalyst yields a greatly enhanced response. The catalyst probably also dissociates the water to some extent. The role of water in this detector is not known. Dagnall *et al.*[15] determined chloride in water solutions with the addition of indium nitrate. They aspirated the chloride–indium nitrate aqueous solution into a cool nitrogen–hydrogen diffusion flame and obtained a limit of detection of *ca.* 0.7 μg/ml. Water has been reported to reduce the emission signal in gas-phase UV fluorescence measurements[17].

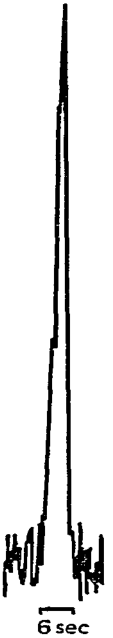
The total consumption burner has advantages over a separate nebulizer and burner. Thus the dead volume and the memory effect are lower. Furthermore a larger proportion of the liquid is consumed. Even completely non-volatile chlorinated compounds are converted using the present burner arrangement.

The optimal conditions for indium in GC detectors, *i.e.*, surface area, temperature, etc., have been reported earlier[11,12].

The temperature of the upper diffusion flame has a strong influence on the formation of indium(I) chloride. The chemical reactions are very complex and little understood. However, it is well known that higher temperatures result in atomization and ionization, and a reduction in the indium chloride signal[15]. The position of the lower burner, as well as the nature of the gas mixture, influence the temperature in the upper flame. These parameters were studied and optimized; the dimensions of the quartz tube were enlarged compared to the earlier GC detectors (Fig. 1).

The limit of detection was determined by injecting chloroform in a water flow of 1 ml/min. The response of the detector is proportional to mass and the limit of detection was calculated at three times the noise as 300 pg/sec (Fig. 3). The detector was linear in the range 0.1–20 μg chloroform injected. The relative standard deviation was 6% (5 μg, $n = 10$).

The selectivity for elemental chlorine is impaired by bromine which has a very weak indium bromide band near 360 nm. The strongest molecular band of indium bromide is 374 nm, which may be used for bromine monitoring analogous to chlorine. Of course other species exhibit emission at 360 nm, however in a continuous flow system these effects are small compared to quenching from organic solvents.



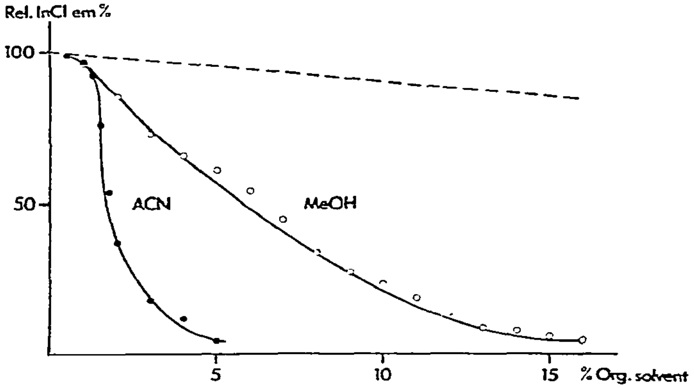


Fig. 3. Detector response of 10 ng chloroform injected in a continuous water flow of 1 ml/min.

Fig. 4. Graph showing the quenching effects of acetonitrile (ACN) and methanol (MeOH) in the HPLC column effluent. The broken line illustrates the dilution of the continuously pumped chloroform-containing (300 ppm) aqueous solution.

Reversed-phase liquid chromatography with the chlorine detector

HPLC in the reversed-phase mode with water–organic solvents is now a widely used technique. The great problem with flame emission detectors is quenching from organic solvents; this was emphasized by Julin *et al.*[7] using a phosphorus–sulphur detector.

The quenching of the indium(I) chloride signal was investigated by use of a gradient of methanol or acetonitrile with a chloroform-containing water solution. With acetonitrile the signal rapidly decreased (Fig. 4). 7% Methanol gave somewhat better results, with a 50% signal reduction. It is clear that the detector cannot be used in the present mode with totally organic mobile phases. The quenching is probably due to radicals formed from the solvent. Chester[8] diminished the quenching effect by decomposition of the organic materials before entry into the HPO formation

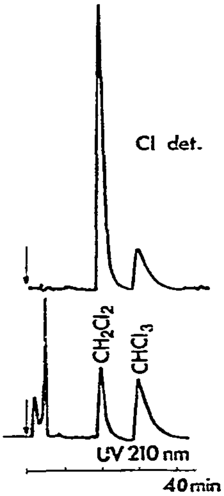


Fig. 5. Separation of dichloromethane and chloroform. Conditions: column (200 × 5 mm I.D.) packed with 5-μm Nucleosil C_{18}; mobile phase, 5% methanol in water, flow-rate 1 ml/min. The chlorine detector and UV detector (210 nm) were connected in series.

region. In our case, this is not possible, since the temperature will be raised, resulting in a reduction in the indium(I) chloride formed.

An attempt to determine chlorophenols with the present detector using a mobile phase of 1% acetic acid, 5% methanol in water was not successful since the chlorine signal completely faded. Another test, with a mobile phase of 5% methanol in water (flow-rate 1 ml/min), was carried out for the separation of dichloromethane and chloroform on a reversed-phase column (Fig. 5). It is interesting to note that the wash-out factor is the same for the UV cell as for the Cl detector. A memory effect is observed with rapidly formed peaks.

With water-based separation systems the chlorine content can be determined successfully.

REFERENCES

1 G. Lunde, J. Gether and B. Josefsson, *Bull. Environ. Contam. Toxicol.*, 13 (1975) 656.
2 R. L. Jolley, *Water Poll. Contr. Fed. J.*, 47 (1975) 601.
3 G. Nota and R. Palombari, *J. Chromatogr.*, 62 (1971) 153.
4 A. T. Chamberlain and J. S. Marlow, *J. Chromatogr. Sci.*, 15 (1977) 29.
5 J. W. Dolan and J. N. Seiber, *Anal. Chem.*, 49 (1977) 326.
6 D. J. Freed, *Anal. Chem.*, 47 (1975) 186.
7 B. G. Julin, H. W. Vandenborn and J. J. Kirkland, *J. Chromatogr.*, 112 (1975) 443.
8 T. L. Chester, *Anal. Chem.*, 52 (1980) 638.
9 P. T. Gilbert, *Anal. Chem.*, 38 (1966) 1920.
10 C. E. Van der Smissen, *U.S. Pat.*, 3,025,141 (1962).
11 C. V. Overfield and J. D. Winefordner, *J. Chromatogr. Sci.*, 8 (1970) 233.
12 M. C. Bowman and M. Beroza, *J. Chromatogr. Sci.*, 9 (1971) 44.
13 B. Gutsche and R. Herrmann, *Z. Anal. Chem.*, 245 (1969) 274.
14 B. Versino and H. Vissers, *Chromatographia*, 8 (1975) 5.
15 R. M. Dagnall, K. C. Thompson and T. S. West, *Analyst (London)*, 94 (1969) 643.
16 R. Belcher, S. L. Bogdanski, Z. M. Kassir, D. A. Stiles and A. Townshend, *Anal. Lett.*, 7 (1974) 751.
17 H. Okabe, P. L. Splitstone and J. J. Ball, *Air. Poll. Contr. Fedr. J.*, 23 (1973) 514.