Journal of Chromatography, 350 (1985) 324–327
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 18 141

Note

Trace analysis of organic compounds in volatile inorganic halides by the dynamic headspace technique and gas chromatography–mass spectrometry

Z. WEIDENHOFFER
Institute of Hygiene and Epidemiology, Šrobárova 48, 100 42 Prague 10 (Czechoslovakia)
and
Z. PLZÁK* and J. DOLANSKÝ
Institute of Inorganic Chemistry, Czechoslovak Academy of Sciences, 250 68 Řež near Prague (Czechoslovakia)
(Received August 30th, 1985)

The volatile chlorides of elements of Groups III–V are widely used in the preparation of ultra-pure materials for the electronics industry. $SiCl_4$, $POCl_3$, $GeCl_4$, BBr_3 and BCl_3 of the highest purity with respect to trace transition elements and –H and –OH molecular impurities are used for the production of optical waveguide glass compositions. The presence of hydrogen-bearing organic and organohalogen impurities in the reactants leads to the undesirable formation of OH groups in fibre-glass during vapour phase oxidation. One of the most suitable methods for the analysis of volatile halides for organic impurities is gas chromatography (GC)[1]. The main problems in the direct GC trace analysis of readily hydrolysable and highly reactive substances, which include most volatile inorganic halides, are the choice of an appropriate liquid stationary phase[2], the low detection limit of the detectors[3] and overloading of the chromatographic column with the matrix substance.

Closed-loop stripping analysis has been successfully applied to the determination of a wide range of volatile organic compounds from a variety of aqueous samples[4]. This pre-concentration technique, capable of achieving concentration factors of up to 5000, makes possible the detection of volatile organic compounds present in aqueous samples at concentrations down to the parts per 10^{12} (ppt) level[5].

This paper demonstrates the use of the dynamic headspace technique for the trace analysis and identification of organic impurities in volatile inorganic halides after their complete hydrolysis in an excess of water.

EXPERIMENTAL

Apparatus

For all experiments a home-made closed-loop stripping device was used. This apparatus differs only in detail from the original instrument designed by Grob and Zürcher[6]. Sorption filters of 3 mm I.D. were filled with charcoal (Aktivkohle für Gaschrom. nach Dr. Grob, 0.05–0.1 mm; Bender-Hobein, Zürich, Switzerland). For

0021-9673/85/$03.30

analytical purposes, filters containing 5 mg of charcoal were used and for purifying water a filter containing 20 mg of adsorbent was employed.

Activation of sorption filters

The filters were rinsed with 2 ml of carbon disulphide followed by 2 ml of acetone before each use. After 15 min under the vacuum of an aspiratory pump, the filters were connected to a nitrogen stream and conditioned for 3 min at laboratory temperature and then for 5 min at 200°C. The flow-rate of nitrogen was 20–30 ml/min. This treatment gave satisfactory filter blanks.

Procedure

A known amount of sample halo compound (usually 5 g) was added dropwise to a sample vessel containing 1000 ml of pre-stripped distilled water. The solution was neutralized by with potassium hydroxide using phenolphthalein as indicator. The sample flask was immediately connected to the stripping apparatus containing a freshly activated charcoal filter. Throughout a 1-h stripping period, a sample temperature of 30°C was maintained. The flow-rate, set by a bellows-pump, was 900 ml/min. After stripping, the sorption filter was repeatedly extracted with 5-μl portions of carbon disulphide. The final extract (total volume *ca.* 20 μl) was transferred into a 100-μl glass capillary vial, sealed and stored at 5°C until taken for the gas chromatographic–mass spectrometric (GC–MS) analysis.

GC–MS analysis

A Hewlett-Packard 5840A gas chromatograph interfaced to a Hewlett-Packard 5985A mass spectrometer with a Hewlett-Packard 21 MX-E computer was employed. The analytical column was a 50 m × 0.32 mm I.D. fused-silica capillary coated with a 0.52-μm film of cross-linked methylsilicone stationary phase (Hewlett-Packard). Injection was by the splitless technique and the oven temperature was programmed from 30 to 200°C. (After isothermal operation at 30°C for 6 min, the temperature was increased to 50°C within 1 min and than programmed with 6°/min to 200°C.) An effluent splitter placed at the end of the chromatographic column was used to divide the effluent between the electron-capture detector of gas chromatograph and the ion source of the mass spectrometer. The quadrupole mass spectrometer was operated in the electron impact mode with an ion source temperature of 200°C, a multiplier voltage of −2400 V and an electron energy of 70 eV. The data system was programmed to scan the analyser from m/z 35 to 320 in 1.1 s.

To obtain information on the concentrations of the impurities present, the total peak area corresponding to impurities in the chromatogram was compared with the peak area of a trichloroethylene standard. For precise quantitation of the different impurities the method described by Graydon *et al.*[7], based on comparison of the areas of the characteristic mass spectrometric peaks, was used.

Materials

$POCl_3$, $GeCl_4$, $SiCl_4$ and BBr_3 of different origins were treated and the contents of organic impurities were compared. Pre-stripped water was produced just in the stripping device. The sample vessel was filled with 1000 ml of distilled water and stripped at 30°C for 1 h using a 20-mg charcoal-filter. The charcoal-filter was than

replaced with an analytical filter (5 mg) and the procedure continued for 15 min. The filter was extracted and analysed immediately. Water of appropriate quality was used for further experiments, otherwise the purification treatment was repeated.

RESULTS AND DISCUSSION

The method described proved to be very effective for the determination of trace amounts of organic impurities contaminating hydrolysable volatile inorganic halides, such as silicon tetrachloride, germanium tetrachloride, boron tribromide and phosphorus oxychloride, because of its simplicity, sensitivity and reproducibility. A chromatogram obtained with the flame ionization detector of the heavily contaminated sample of $GeCl_4$ is shown in Fig. 1. A total content of impurities of 75 mg/kg was found. In the sample 47 compounds, mostly chloro and bromo derivatives of alkanes, olefins and aromatics, were identified.

The purity of standard quality commercial $POCl_3$ is demonstrated by Fig. 2. The impurities consisted mainly of perchloroalkanes, a total content of 2 mg/kg being found.

The sensitivity of the method is determined by characteristics of the GC–MS system used. When 2 μl of carbon disulphide extract (10% of the total volume) were injected into the gas chromatograph and when 25 ng of a component are needed for the identification, the starting sample (5 g) should contain at least 250 ng of each impurity. In this instance, the sensitivity limit is 0.05 mg/kg, which is satisfactory for the present application. A further increase in sensitivity can be achieved by increasing

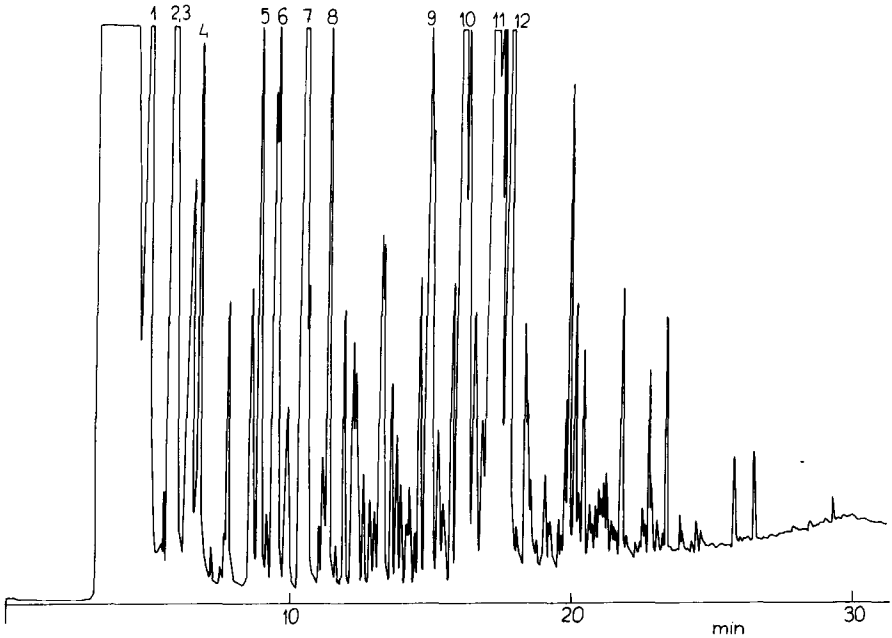

Fig. 1. Chromatogram of organic impurities in $GeCl_4$. 1 = Trichloromethane; 2 and 3 = benzene and tetrachloromethane; 4 = trichloroethylene; 5 = toluene; 6 = bromodichloroethylene and dibromochloromethane; 7 = tetrachloroethylene; 8 = chlorobenzene and 1,1,1,2-tetrachloroethane; 9 = methylethylbenzene; 10 = dichlorobenzene; 11 = diethylbenzene; 12 = hexachloroethane.

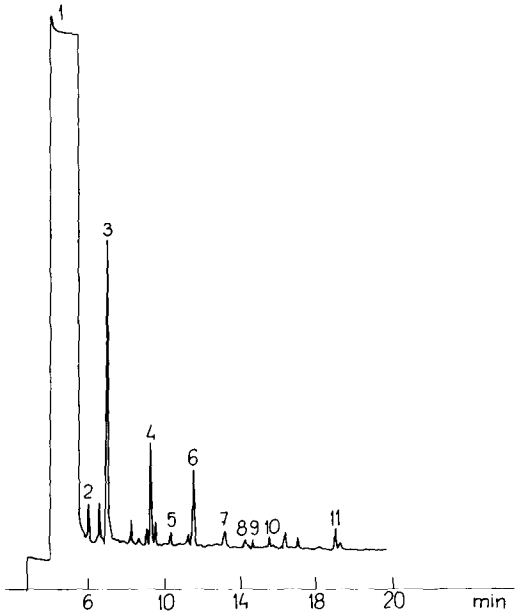

Fig. 2. Chromatogram of organic impurities in electronic-grade $POCl_3$. 1 = Solvent peak; 2 = trichloromethane; 3 = tetrachloromethane; 4 = 1,1,2-trichloroethane; 5 = 1,2,2-trichloropropane; 6 = 1,1,1,2-tetrachloroethane; 8 = 1,1,2,2-tetrachloropropane; 9 = 1,1,2-trichloropropene; 10 = pentachloroethane; 11 = hexachloroethane.

the amount of the starting sample and/or by utilizing the closed-loop stripping technique with thermal desorption of the filters[7], which avoids dilution of the sample by the solvent.

REFERENCES

1 H. Rüssel and G. Tölg, *Top. Curr. Chem.*, 33 (1972) 1.
2 G. Parissakis, D. Vranti-Piscou and J. Kontoyannakos, *J. Chromatogr.*, 52 (1970) 461.
3 Y. A. Saprykin, B. M. Golovko and Y. A. Pazderskii, *J. Chromatogr.*, 246 (1982) 51.
4 R. G. Melton, W. E. Coleman, R. W. Slater, F. C. Kopfler, W. K. Allen, T. A. Aurand, D. E. Mitchell, S. Y. Voto, S. V. Lucas and S. C. Watson, in L. H. Keith (Editor), *Advances in the Identification and Analysis of Organic Polutants in Water*, Vol. 2, Ann Arbor Sci. Publ., Ann Arbor, MI, 1981, p. 597.
5 J. Curvers, Th. Noy, C. Cramers and J. Rijks, *J. Chromatogr.*, 289 (1984) 171.
6 K. Grob and F. Zürcher, *J. Chromatogr.*, 117 (1976) 285.
7 J. W. Graydon, K. Grob, F. Zürcher and W. Giger, *J. Chromatogr.*, 285 (1984) 307.