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GAS CHROMATOGRAPHIC ANALYSIS OF VOLATILE CHLORIDES FOR ORGANIC AND ORGANOCHLORINE IMPURITIES USING A HIGH-FREQUENCY EMISSION DETECTOR

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SUMMARY

A high-frequency emission detector was applied in the gas chromatographic analysis of volatile silicon and germanium chlorides for organic and organometallic impurities. The dependence of the detector response on the discharge tube pressure, carrier gas flow-rate and the slit width of the monochromator was studied. Optimum operating conditions were found to be pressure of the discharge tube, 30–50 mmHg; slit width of the monochromator, 0.12–0.15 mm; and carrier gas flow-rate, 30–40 ml/min. The linearity, selectivity and sensivity of the detector for some carbon-containing materials were studied. The linear range of the detector was not less than 10^4. The selectivity towards carbon-containing materials present in silicon and germanium chlorides is about 10^3. The detection limit is $1 \cdot 10^{-5}$–$1 \cdot 10^{-4}$ mol %.

INTRODUCTION

The volatile chlorides of the elements of Groups III–V are widely used in the preparation of ultra-pure materials for the epitaxial growth and doping of films and in the preparation of fibre guides. One of the most suitable methods for the analysis of volatile chlorides for organic and organochlorine impurities is gas chromatography. However, the analysis of readily hydrolysable substances, to which most volatile chlorides belong, involves many difficulties, such as the choice of the detector[1,2].

The katharometer, gas density balance, flame-ionization detector, electron capture detector and thermionic detector are usually used for the analysis of aggresive materials. The katharometer and gas density balance are not sufficiently sensitive and therefore cannot be used for the detection of impurities when present at levels below 10^{-3}–10^{-2} % without preliminary enrichment. A flame-ionization detector is highly sensitive and has a wide linear range. However, the analysis of volatile chlorides using a flame-ionization detector is difficult, as non-volatile products of chloride hydrolysis are deposital on the detector electrodes and insulators and disturb the stability of the detector operation and decrease its sensitivity. In addition, the flame-ionization detector is not sensitive to some compounds, such as carbon dioxide, carbon monoxide and carbon oxychloride.

The application of electron-capture and thermionic detectors to the analysis of volatile chlorides for organic impurities is complicated by the fact that their sensitivity to chlorine-containing compounds is substantially higher than that to organic compounds.

Therefore, when the main constituent (a volatile chloride) enters the detector, the detector saturation of the detector and a decrease in its sensitivity to organic materials occur.

McCormack *et al.*[3] used a high-frequency emission detector and measured the specific wavelength emission of the elements entering the microwave electrodeless discharge in argon.

This method was used successfully for the determination of herbicides and insecticides in products of vegetable and animal orgin[4] and of fixed gases[5]. The possible applications of the detector to different types of the electric discharge[6] have been studied using the vacuum range of the UV spectrum[7].

The object of this work was to study the application of the high-frequency emission detector to the analysis of volatile chlorides for organic and organochlorine impurities.

EXPERIMENTAL

The scheme of the chromatographic assembly, consisting of a Tsvet-110 chromatograph and ISP-51 spectrograph with an FEP-1 photoelectric recorder is shown in Fig. 1. The discharge tube with a diameter 12 mm was of made molybdenum glass.
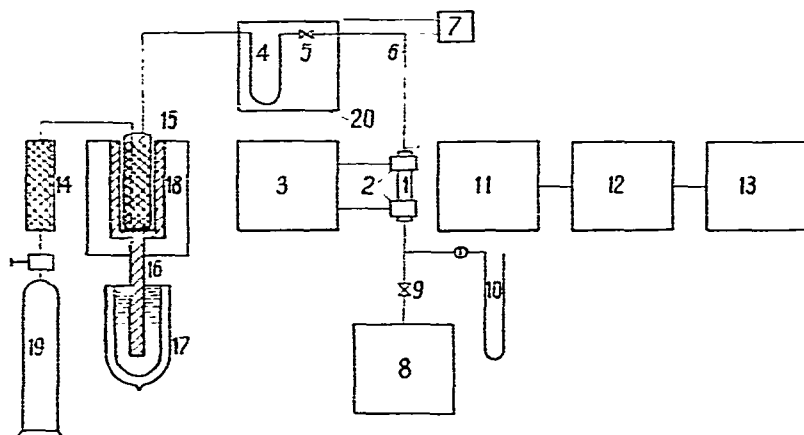

Fig. 1. Schematic diagram of the chromatographic assembly.

Copper annular electrodes (2) with a wall thickness of 0.5 mm, electrode widths of 10 mm and a distance between them of 20 mm were used. The electrodes were connected with a UVCH-66 high-frequency generator (3) by a coaxial cable. The frequency of the generator was 40 MHz and the output power was 70 W. To eliminate vacuum formation in the chromatographic column (4), at the exit of the latter a valve (5) was mounted in the column thermostat and the capillary tubing (6) was heated

electrically by a separate regulated power supply (7) to prevent condensation of the sample components.

The other end of the discharge tube was attached to a VN-461 vacuum pump (8). The pressure in a discharge tube was established by means of the valve (9) and was controlled by a mercury manometer (10).

The discharge tube (1) is placed 40 mm from the monochromator entrance slit (11). The operating wavelength region is 3600–6600 Å. The measuring unit of the photoelectric recorder was not used. The photomultiplier at the exit was connected to an IMT-0.5 d.c. amplifier (12) from the Tsvet-110 chromatograph. The limits of the measurement and of the internal current compensation were extended to $1 \cdot 10^{-4}$ and $4 \cdot 10^{-7}$ A, respectively. A KSP-4 self-recording potentiometer (13) was used as the recorder.

Argon used as the carrier gas was purified by passing it through NaA and NaX molecular sieve traps. The NaA trap was cooled with liquid nitrogen. To prevent condensation of argon in the trap (15), the latter was placed in a copper cylinder (16), the lower end of which was immersed in the vessel containing the liquid nitrogen. The temperature in the upper part of the cylinder exceeded the argon condensation temperature at the expense of the heat transmission resistance. Regeneration of the molecular sieve was carried out by heating under vacuum for 6–8 h at 300–350°C. Glass chromatographic columns 1 and 5 m long and 3 mm I.D. were used. The dependence of the detector response on the discharge tube pressure, carrier gas flow-rate and slit width of the monochromator was studied using a 1-m column packed with polymeric Polysorb-1 (0.25–0.5 mm). The column was conditioned for 24–28 h in the carrier gas flow at 250°C and operated at 110°C. The sample size was 1 ml, introduced with a syringe.

For the study of the sensitivity, linearity and selectivity of the detector and for the analysis of volatile chlorides, a 5-m column was used, packed with 8 % Lucopren on a Teflon support. The column was conditioned for 24–28 h in a carrier gas flow at 150°C. The operating column temperature was 70°C and the temperature of the evaporator was 120°C. Samples were injected with a 10-μl glass syringe.

Carrier gas flow-rates were measured by means of a soap-bubble flow meter attached to a capillary tube (6).

A standard mixture with a constant composition of carbon tetrachloride vapour in argon was prepared by the diffusion-dynamic method[8]. Standard mixtures for the study of the selectivity, linearity and sensitivity were prepared by diluting the mixture to be analysed with ultra-pure silicon chloride.

RESULTS AND DISCUSSION

The high-frequency discharge in argon was excited at a pressure of the discharge tube below 10–15 mmHg. At higher pressures a discharge was initiated by means of a Tesla transformer. After the discharge had been initiated, its steady state was maintained by increasing the pressure to 150–200 mmHg. With increasing pressure the plasma narrowed and separated from the surface of the discharge tube. An increase in pressure to 250–300 mmHg resulted in extinction of the discharge, apparently owing to the insufficient high-frequency energy contributed to the discharge.

The effect of the sample on the discharge varied depending on the pressure of

the discharge tube. At pressures of 5–10 mmHg the discharge was not extinguished by liquid samples of silicon and germanium chlorides with volumes of 10 μl. However, with the multiple injection of large samples of chlorides on the inside of the discharge tube a coating was formed, which decreased the light transmission of the discharge tube. At pressures of 30–50 mmHg sample sizes that did not cause extinction of the discharge were decreased to 0.5–1 μl, but the formation of a coating on the inside of the discharge tube was slowed.

The emission spectrum of the high-frequency discharge plasma in argon containing some organic materials has many lines and bands emitted both from atoms and fragments of molecules such as CN, C_2 and CH[3]. The highest sensitivity of the detector to carbon-containing materials could be obtained by using the CN band at 3883 Å for detection. Therefore, all studies on the high-frequency emission detector used for work with chlorides were performed by setting the monochromator at 3883 Å.

To select the optimum pressure of the discharge tube the relationship of the detector response to identical samples of carbon tetrachloride at various discharge tube pressures was determined. This relationship is shown in Fig. 2, which indicates that the maximum detector response was observed in the pressure range 30–50 mmHg.
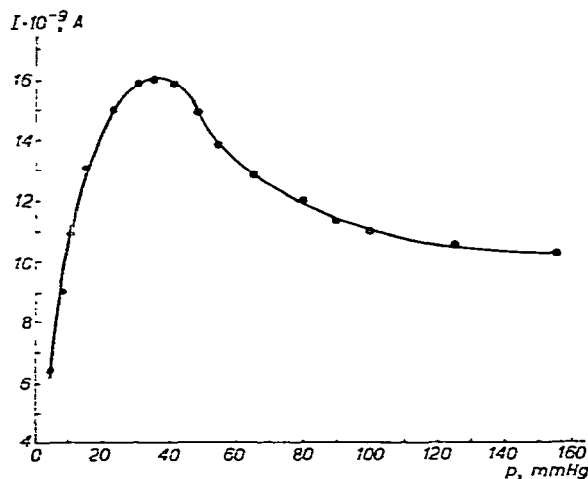

Fig. 2. Detector response *versus* discharge tube pressure.

A graph of the detector response against carrier gas flow-rate at a constant pressure of the discharge tube is shown in Fig. 3. This curve is different in form if the sample is injected directly into the discharge tube and if the sample is injected into the chromatographic column. In the former instance (curve 1) the response was not dependent on the carrier gas flow-rate, whereas in the latter instance curve 2 apparently reflects the tailing of the chromatographic peak in the column depending on the carrier gas flow-rate.

An important factor influencing the sensitivity and selectivity of the detector is the slit width of the monochromator. To select the optimum slit width the relation-
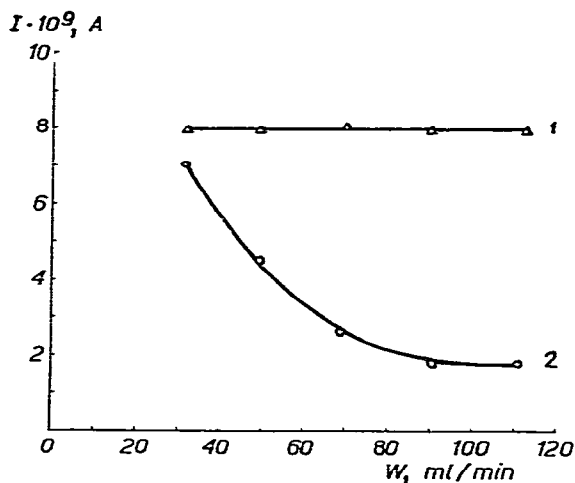
Fig. 3. Detector response *versus* carrier gas flow-rate.

ship between the signal-to-noise ratio and the monochromator slit width was de-
termined. The entrance and the exit slit widths were chosen to be identical. As can be
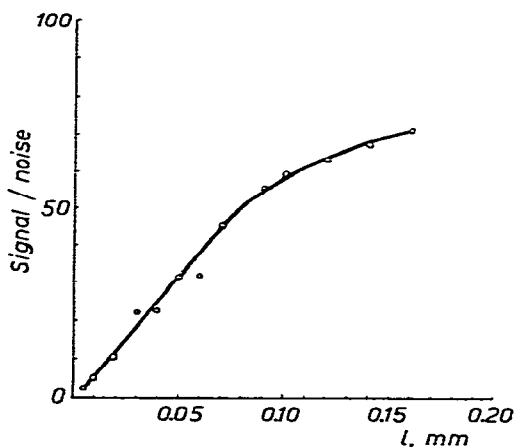seen in Fig. 4, the signal-to-noise ratio increased with increase in slit width.

Fig. 4. Signal-to-noise ratio *versus* slit width of the monochromator.

The peak height of carbon tetrachloride was 1000 times greater than that of
silicon and germanium tetrachlorides. A slit width of 0.12 mm was used in this work;
with a decrease in the slit width the selectivity increased and the sensitivity decreased.

The logarithmic relationship between the detector response and the component
concentration is shown in Fig. 5, and indicates that in the range of concentrations
studied $(1 \cdot 10^{-5}$–$1 \cdot 10^{-1}$ mol %)the detector response is linear. The sensitivity of the
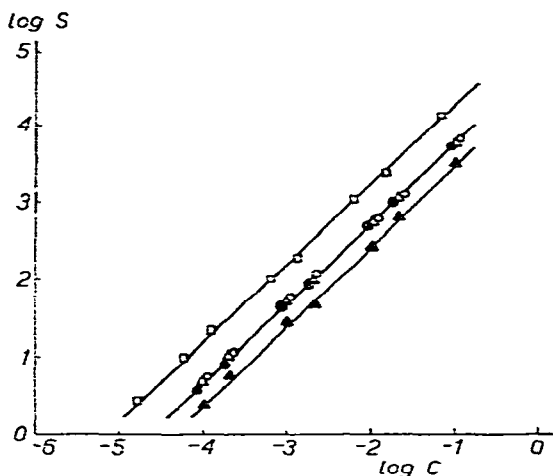detector was dependent on the number of carbon atoms in the molecule.

Fig. 5. Logarithm of peak area *versus* logarithm of component concentration.

TABLE I

DETECTION LIMITS OF ORGANIC IMPURITIES IN THE ANALYSIS OF SILICON AND GER-MANIUM CHLORIDES USING A HIGH-FREQUENCY EMISSION DETECTOR

Impurity	Limit of sensitivity $(mol\%)$
Pentane	$1.5 \cdot 10^{-5}$
1,1-Dichloroethane	$5 \cdot 10^{-5}$
1,2-Dichloroethane	$5 \cdot 10^{-5}$
1,1,1-Trichloroethane	$5 \cdot 10^{-5}$
Carbon tetrachloride	$1 \cdot 10^{-4}$

The detection limits (peak height twice the noise level) of some organic compounds are given in Table I.

It should be noted that the detection limit depends on the volatility of the stationary phase if a high-frequency emission detector is used. Therefore, the data in Table I may be improved by using a less volatile stationary phase or by using lower temperatures for the chromatographic separation.

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