

CHROM. 13,280

MONITORING OF AGGRESSIVE COMPONENTS BY MEANS OF A SIMPLE CORROSION-RESISTANT ALL-GLASS PROCESS GAS CHROMATOGRAPH WITH AN ARGON PLASMA DETECTOR

A. KUESSNER

BASF AG, Ludwigshafen (G.F.R.)

SUMMARY

A corrosion-resistant gas chromatograph is described for the analysis of aggressive gaseous compounds (HCl, Cl₂, COCl₂, NO₂, etc.) in any gas mixtures or of inert compounds (as vinyl chloride) in aggressive media, even in the presence of water. The detection is based on an electrodeless plasma discharge in argon as the carrier gas. As all surfaces in contact with the sample gas consist of glass or PTFE, stability against corrosion could be achieved.

Disadvantages of this detector are the limited dynamic range of approximately three decades and the individuality of each discharge tube; individual calibration graphs are required. Advantages are the corrosion resistance and consequently the constancy of sensitivity over several years of maintenance-free process operation.

INTRODUCTION

For the determination of aggressive gases such as HCl, Cl₂, COCl₂ and NO₂, normally chemical or physico-chemical methods are used. Gas chromatography (GC) has not been applied very widely, and the literature is sparse¹⁻⁴. The problem is mainly the corrosion that occurs on all metallic surfaces that come into contact with the sample gases, especially if in a prolonged process operation traces of water cannot be excluded.

For operation in chemical plants working with corrosive gases such as HCl and COCl₂ some simple and rugged and maintenance-free gas chromatographs were desired. A requirement was that no metallic surfaces should come into contact with the sample gas.

For the gas inlet commercial magnetic valves are readily available, the tightening parts of which consist of PTFE (Convac, Serres, G.F.R.). Separation columns made of glass with inert supports and stationary phases also are well known (*e.g.*, Fluorolube on Chromosorb T). The real problem was to obtain a corrosion-resistant detector.

A GC detector that really avoids metallic surfaces coming into contact with the sample gas is the plasma discharge detector with electrodeless excitation. In contrast to all molecular gases, the monatomic noble gases can be excited by electric fields to give plasma discharges even at ambient pressure. This excitation can be

effected by the capacitive transfer of a sufficiently high and sufficiently high-frequency alternating voltage through the isolating wall of an appropriate discharge tube. If pure argon is used as the carrier gas in a gas chromatograph, it can be excited to give a plasma discharge when leaving the separation column. Any concentration profile in this argon will influence this plasma, and any method for measuring the extent of this influence is a method for quantitative detection.

Plasma discharge detectors based on this principle, using frequencies between 100 and 2500 MHz, are well known⁵⁻⁷. Their electronics are expensive and this precludes their application for the desired simple and cheap surveillance instruments. However, another approach seemed feasible. The capacitive charge transfer is proportional to both frequency and voltage and higher voltages allow lower frequencies, so that the electronics should be simpler and cheaper.

The transfer of the signal to the recording system also must be effected by capacitive charge transfer. The compounds of interest will be completely ionized in the plasma and so increase its conductivity. Variations in the voltage drop along the plasma discharge should be transferred to a coil around the discharge tube.

EXPERIMENTAL

Fig. 1 shows the assembly developed. The output of a 10-kHz frequency generator circuit was amplified by an HC 1000 high-performance transistor and fed into an ordinary ignition coil of a car engine. The resulting voltage of *ca.* 10 kV was sufficient to excite a plasma discharge in argon after an electrodeless charge transfer. Owing to the high inductance of the ignition coil it is unimportant whether the original alternating voltage has a sine, rectangular or triangular shape.

The length of the discharge tube is 160 mm, and in the centre of this quartz tube a supplementary electrode is attached. This is a metal wire (*ca.* 30 mm long, 0.1 mm diameter, preferably steel), protected by a thin quartz capillary which is closed at the front end. It is positioned in the centre by a glass plunger and is displaceable

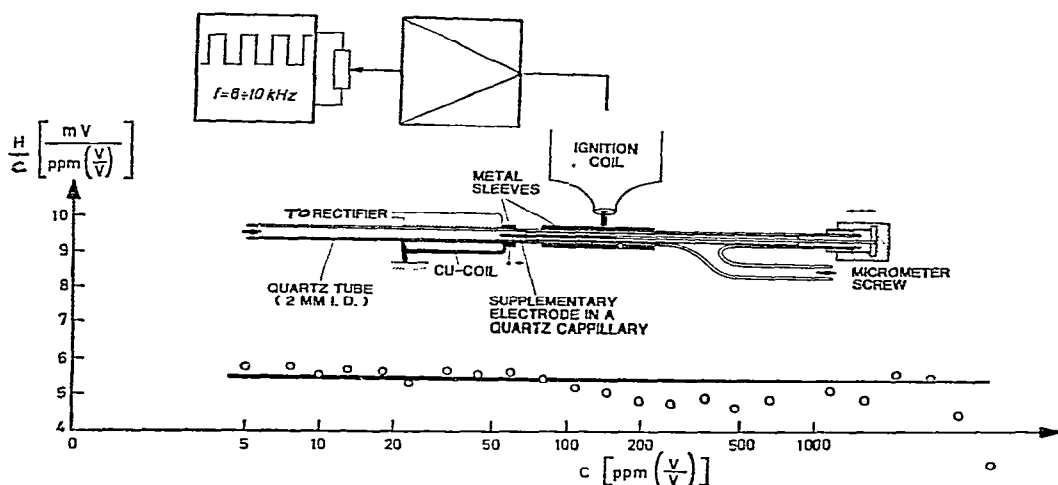


Fig. 1. Discharge tube and sensitivity diagram.

in the axial direction by a micrometer screw. The correct position of this supplementary electrode relative to the outer coverings is essential for the detector performance, and must be optimized once at the beginning of the operation.

The signal coil consists of *ca.* 100 turnings of an isolated copper wire of diameter 0.17 mm, fixed by a thin layer of two-component resin. The transferred signal voltage is rectified by an ordinary measuring rectifier of an adjustable coil a.c. meter [copper(I) oxide diodes in a Graetz circuit] or by a specially constructed circuit in order to avoid non-linearity at low values. The first method is simpler, but requires a non-linear calibration graph. The signal voltage output goes up to 100–200 mV.

The electronics consist of semiconductor elements, the performance of which depends on temperature. To make use of the stability of the sensitivity the whole assembly has to be kept at constant temperature. The chromatograph with all supplementary devices (inlet valves, timer, column, detector) is housed in a plastic box (40 × 50 × 60 cm), the interior of which is maintained at *ca.* 45°C. The stability of the sensitivity allows the application of a bar graph technique for recording the results (see Fig. 2).

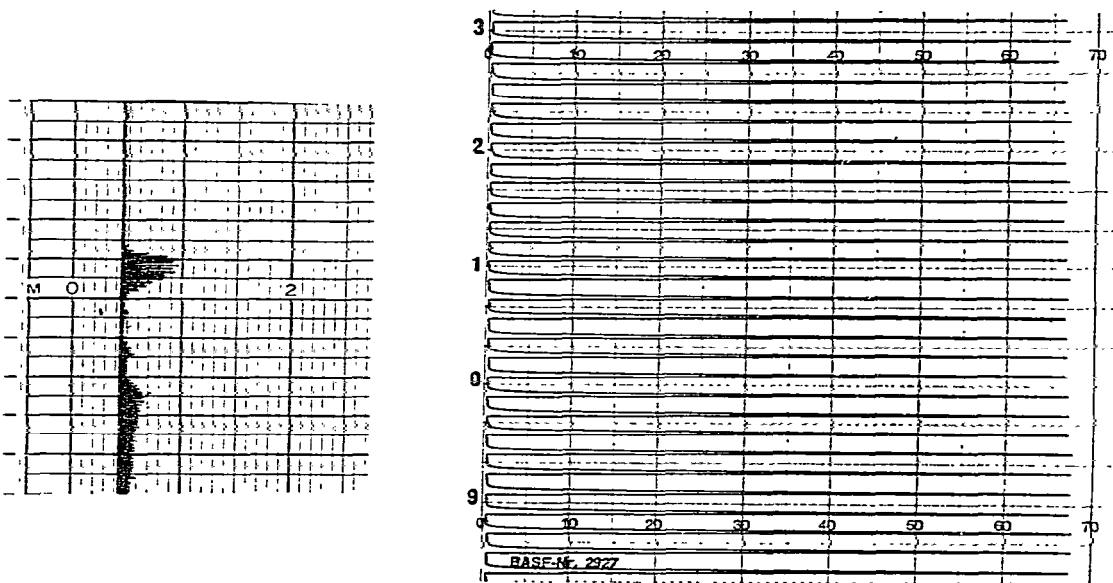


Fig. 2. Example of bar graph and reproducibility test.

RESULTS

After separation in an appropriate separation column, all of the aggressive gases mentioned give rise to ordinary GC peaks. The reproducibility is *ca.* 5% relative. The dynamic range extends over approximately three decades of concentration. The calibration graph in Fig. 1 was obtained by an automatic logarithmic dilution procedure. Each discharge tube has to be calibrated individually. Differences may result from different distances of the covering electrodes and the shape of the closing tip of the capillary of the supplementary electrode. Deviations from linearity

of 20–30% may occur as can be seen in Fig. 1), but these are reproducible, which means that they can be corrected by using an appropriate calibration graph. For most industrial monitoring purposes, especially regarding exhaust gases, they are unimportant.

The detection limit corresponds to *ca.* $5 \cdot 10^{-10}$ g sec⁻¹ of chlorine.

The advantage of this detector is its resistance to chemical attack. The mentioned reproducibility has been observed over a period of 2 years of continuous process operation.

DISCUSSION

In the well known noble gas detector⁸, ions are formed by the interaction of excited metastable noble gas atoms with the neutral molecules to be detected. This mechanism cannot be valid in the present instance. The highest excited metastable state of argon has an energy of 11.72 eV, while we find carbon monoxide (14.01 eV) and carbon dioxide (12.34 eV) still detected.

The ionization energy of argon is 15.76 eV. Up to this limit, ionization processes by particle collisions or by internal photoionization processes should be possible. On the other hand, methane (12.98 eV) and nitrogen (15.51 eV) are not detected. A possible explanation of this apparent contradiction might be to accept primary energy transfer processes by collisions with high-energy particles in competition with bimolecular deactivation processes⁹. The failure to detect nitrogen and methane may be the result of a longer lifetime of activated but not yet ionized molecules and atoms (according to the Lindemann–Hinshelwood mechanism). This concept is supported by the observation that at decreasing pressures in the discharge tube ($p \leq 300$ mbar) signals for nitrogen and methane begin to appear. These considerations are equally applicable to the assumption of an internal photoionization process¹⁰.

A detailed investigation has not been carried out, but it would be of only theoretical interest. The use of a vacuum pump would be an unacceptable complication in the described simple unit. Further, all of the compounds of interest can be easily detected at ambient pressure.

REFERENCES

- 1 V. F. Sukhoverkhov, L. G. Podzolko and V. F. Garanin, *J. Anal. Chem. U.S.S.R.*, 30 (1975) 274–277.
- 2 R. M. Bethea and M. C. Meador, *J. Chromatogr. Sci.*, 7 (1969) 655–664.
- 3 H. Runge, *Z. Anal. Chem.*, 189 (1962) 111.
- 4 J. F. Ellis and G. Iveson, in D. H. Desty (Editor), *Gas Chromatography*, Butterworths, London, 1958, p. 300.
- 5 W. R. McLean, in D. R. Hodges (Editor), *Recent Analytical Developments in the Petroleum Industry*, Applied Science, Barking, 1974, pp. 139–167.
- 6 P. Lacaze, *Chromatographia*, 6 (1973) 32–38 and 12 (1979) 803–807.
- 7 D. Jentzsch and E. Otte, *Detektoren in der Gas-Chromatographie*, Akademische Verlagsgesellschaft, Frankfurt, 1970, p. 373.
- 8 D. Jentzsch and E. Otte, *Detektoren in der Gas-Chromatographie*, Akademische Verlagsgesellschaft, Frankfurt, 1970, p. 207.
- 9 J. Ševčík and S. Krýsl, *Chromatographia*, 6 (1973) 375–380.
- 10 J. N. Discoll and J. B. Clarici, *Chromatographia*, 9 (1976) 567–570.