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GAS CHROMATOGRAPHIC DETECTION OF SO₂, NO₂, AMINES AND HALOCARBONS USING AN AEROSOL IONIZATION DETECTOR*

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SUMMARY

The highly specific aerosol ionization detector primarily serves to detect halocarbons and basic or acid reacting compounds. The advantages and disadvantages of this detector for the determination of SO₂, NO₂, amines and halocarbons were studied. Applications of the detector in the fields of air pollution measurement and of the monitoring of the air at workplaces are described. Detection limits are given and possibilities of a further improvement of the sensitivity are discussed.

INTRODUCTION

The aerosol ionization detector (AID) developed by Popp *et al.*[1-3] has proved suitable for a selective and sensitive detection of substances or groups of substances. The principle of this detector was described earlier[3]. Aerosols from basic reacting compounds are formed by reaction with trifluoroacetic acid[4], aerosols from acidic reacting compounds by reaction with amines[5-7], aerosols from halocarbons by reaction with hot copper oxide[6-8] and those from metallorganic compounds by pyrolysis[7,8]. A combination of these reactions (*e.g.* oxidation of SO₂ to SO₃ by means of an oven and subsequent reaction with amines) is also possible.

This paper describes the possibilities of the AID for the determination of SO₂, NO₂, amines and halocarbons, pointing out its advantages and disadvantages with respect to the various modes of operation.

THEORETICAL

A theoretical model[3] of the processes occurring in an AID is analogous to the studies of Wentworth *et al.*[9-11] for the electron-capture detector (ECD). The authors[3] showed that the relation

$$\Delta i / i_0 - \Delta i = K^* \cdot a$$

where Δi = decrease of the ionization current in the presence of aerosols, i_0 = basic ionization current, K^+ = constant defined in analogy to the electron capture coefficient and a = concentration of sample molecules is also valid for the AID.

Theoretical studies by Grosse[12] for continuously working aerosol ionization analyzers, especially for the ionization chamber using an internal radiation source, provided the relation

$$\frac{\Delta i}{i_0 - \Delta i} \cdot \frac{1}{\Delta(\beta Z)} = -\left[\sqrt{\frac{aq}{1 - i_0/i_s}}\left\{2 - \frac{i_0}{i_s}\left(1 - \frac{i_0}{i_s}\right)\right\} + \beta Z\right]^{-1}$$

where i_s = saturation current, α = ion–ion recombination coefficient, β = attachment coefficient of ions to aerosols, Z = number of aerosol particles per unit volume and q = number of ions formed per unit time and volume.

Grosse defined the sensitivity, S, of an AID to be the quotient of the change, Δi, of the ionization current and the change, $\Delta(\beta Z)$, of the value which is characteristic of the aerosol particles.

Assuming small concentrations of aerosols, S is approximately equal to the expression

$$\frac{i_0}{\sqrt{aq}} \; \frac{\sqrt{1 - i_0/i_s}}{2 - i_0/i_s}$$

The maximum sensitivity is reached with $i_0/i_s = 0.76$. Using the d.c. mode of AID operation this ratio should be noted.

EXPERIMENTAL

Fig. 1 shows the principle of an AID with a reaction oven. The oven is slid over the unfilled end of the quartz gas chromatographic column or over a small quartz tube connecting the column and the detector of such a size that the dead volume between the column packing and the ionization chamber is less than 1 ml. The quartz tube contains a copper pin, diameter less than 3 mm and length 2 mm. At oven temperatures of 900–980°C, the halocarbons to be analysed are converted
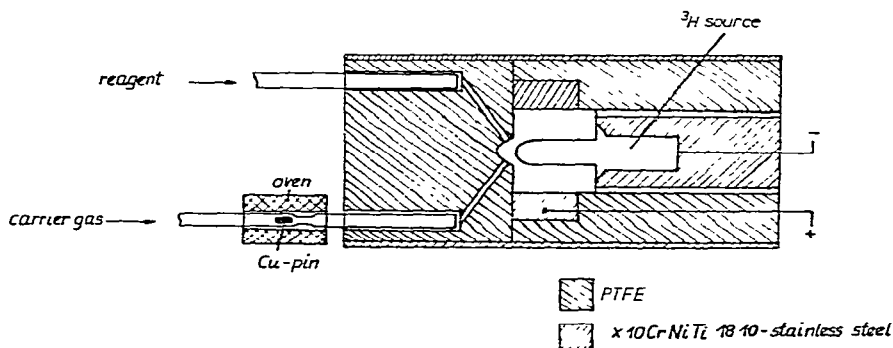

Fig. 1. Scheme of the AID.

into aerosols. The determination of SO_2 takes place at temperatures of *ca.* 900°C (without copper pin) and with the addition of a basic reagent; the acid and basic reacting compounds are determined without heating and with the column filled by the addition of amines and trifluoroacetic acid, respectively. In each case air is used as carrier gas. This has two advantages: (i) the ECD mode of operation cannot affect the selectivity and the sensitivity of the AID; (ii) it is possible to inject large sample volumes without the occurrence of troublesome air peaks.

The detector has a concentric tube geometry, and the radiation source (^3H, ^{63}Ni or ^{85}Kr) serves as an internal electrode. The experiments described in this paper have been performed with an ^3H source. The detector worked in the d.c. mode of operation with a ratio $i_0/i_s = 0.7$ and was inserted in an environmental gas chromatograph constructed at the Central Institute for Isotope and Radiation Research, Leipzig[13,14].

RESULTS AND DISCUSSION

Determination of halocarbons

Halocarbons (especially chloro- and fluoro-containing compounds) are determined by conversion into copper chloride aerosols at 900–980°C, *e.g.*:

$$C_2HCl_3 + CuO \rightarrow CuCl_2 + products$$
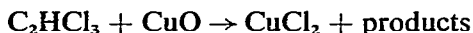
In comparison to the ECD, the AID has the advantage that chloro and fluoro compounds with one or two halogen atoms can also be determined with detection limits in the ppb range; the disadvantage lies in the lower sensitivity compared with the sensitivity of the ECD for CCl_4, pesticides and some other compounds. Bromides are detected with a lower sensitivity than chlorides and fluorides and iodides are undetectable. Fig. 2 shows the connection between the quotient $\Delta i/i_0 - \Delta i$ and the concentration, *a*, of the sample (in this case Freon 12). The AID has a dynamic range (this applies to all modes of operation) of *ca.* 10^2. After a sharp bend there is an extended range in which there also exists a linear connection between $\Delta i/i_0 - \Delta i$ and *a*. With adequate calibration we used both regions for measurements.

The detection limits for the following halocarbons determined with the AID lie between 100 ppb* and 500 ppb: ethyl chloride, allyl chloride, *n*-butyl chloride, Freon 12, methylene chloride, *n*-propyl chloride, halan, tetrachloromethane, tetrachloroethane, trichloroethylene. If amines are added behind the reaction oven (in this case the temperature of the detector must not exceed 60°C) it is possible to reach detection limits of *ca.* 10 ppb.

Fig. 3 shows the chromatogram of a sample with 100 ppm of Freon 12, CCl_4 and C_2HCl_3.

Determination of SO₂

The determination of SO_2 was performed at temperatures of *ca.* 900°C and subsequent reaction with a basic reacting compound (*n*-propylamine):

$$SO_2 + 1/2\ O_2 \longrightarrow SO_3\ \text{(oxidation)}$$
$$SO_3 + 2\ RNH_3 + H_2O \rightarrow (RNH_3)_2SO_4$$

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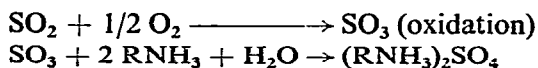
* Throughout this article the American billion (10^9) is meant.
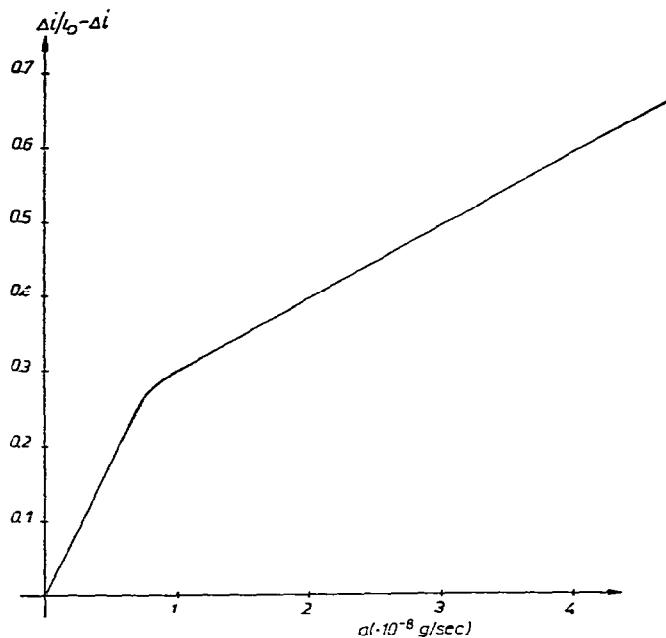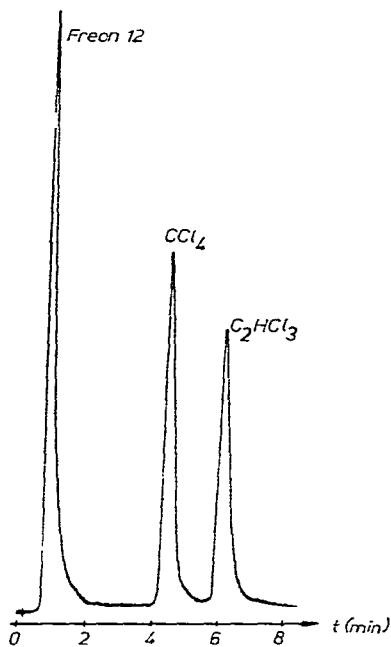
Fig. 2. Linearity of the AID. Sample: Freon 12.

Fig. 3. Analysis of halocarbons in air. Column: 2 m × 4 mm I.D., glass, 10% SE-30 on Chromo-sorb W AW DMCS. Temperatures: column, 30°C; oven: 960°C. Sample size: 50 μl with 100 ppm Freon 12, CCl₄ and C₂HCl₃.

The concentration of *n*-propylamine in the ionization chamber of the AID was 20 ppm. With this arrangement it was possible to detect 200 ppb of SO_2 in a 10-ml air sample.

Fig. 4 shows a chromatogram of 1 ml of air containing 5 ppm SO_2. A short deactigel column was used.
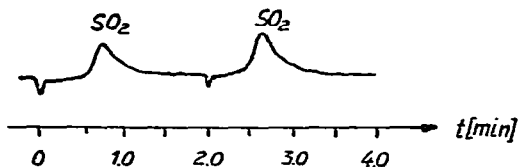

Fig. 4. Determination of SO_2. Column: 25 cm × 4 mm I.D., glass, deactigel. Carrier gas: air. Temperatures: 130°C; oven, 900°C. Concentration of amine: 20 ppm. Sample size: 1 ml air with 5 ppm SO_2.

Air pollution measurements of SO_2 are possible using a cooled pre-column for sample enrichment. With deactigel as column packing no substance passing the column except H_2S causes a detector signal.

The detection limit of the AID in this mode of operation (and also in the others) can be improved by radioactive sources with a higher saturation current (in our case 10^{-9} A), so that an air pollution control without enrichment seems to be possible.

Determination of NO₂ and amines

The determination of NO_2 and amines with the AID is simple in so far as the reaction oven is unheated and only the corresponding reagent diffuses into the ionization chamber of the detector. Yet there are the following difficulties:

(1) For the determination of basic reacting compounds it is necessary to avoid column packings with basic reacting liquid phases. Similarly, for the determination of acid reacting compounds, packings with acidic reacting liquid must be avoided because bleeding causes a strong decrease of the basic ionization current and as a result a decrease of the sensitivity.

(2) The gas–gas reaction which leads to the formation of aerosols can be used only for temperatures below 60°C; higher temperatures cause a change of the steady state in favour of the initial substances. Thus the determination of amines with Chromosorb 103 as column packing makes it necessary to work with a hot column and cold detector, but this may lead to the condensation of the substances in the ionization chamber.

The following two examples show the detection of NO_2 and amines. Fig. 5 shows the determination of NO_2 in a glass blower's workshop with sample enrichment. The column, cooled to −78°C, served for sample enrichment from 130 ml of air. When the column was warmed the NO_2 peak and an asymmetric water peak appeared. Without enrichment a detection limit of 250 ppb (related to a 10-ml sample) was achieved with this arrangement.

Fig. 6 shows the detection of amines in air using Chromosorb 103 as column packing and with the column and the detector at different temperatures. The best results were obtained with a 95:5 mixture of nitrogen and oxygen as carrier gas. The oxygen peak is due to this carrier gas. Further studies with amines are in preparation.
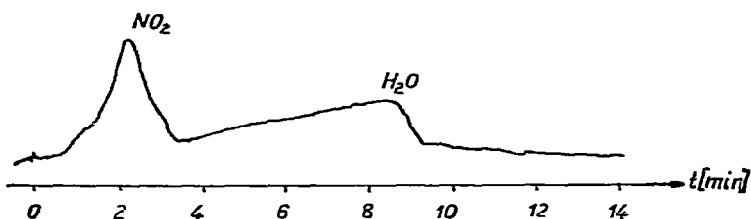
Fig. 5. Analysis of NO_2 in a glass blower's workshop. Column: 1 m × 4 mm I.D., PTFE, 10% Fluorolube-oil on Fluoropak 80. Temperature: 30°C. Concentration of amine: 100 ppm. Sample size: NO_2 enriched from 130 ml. NO_2 room concentration: 1 ppm.
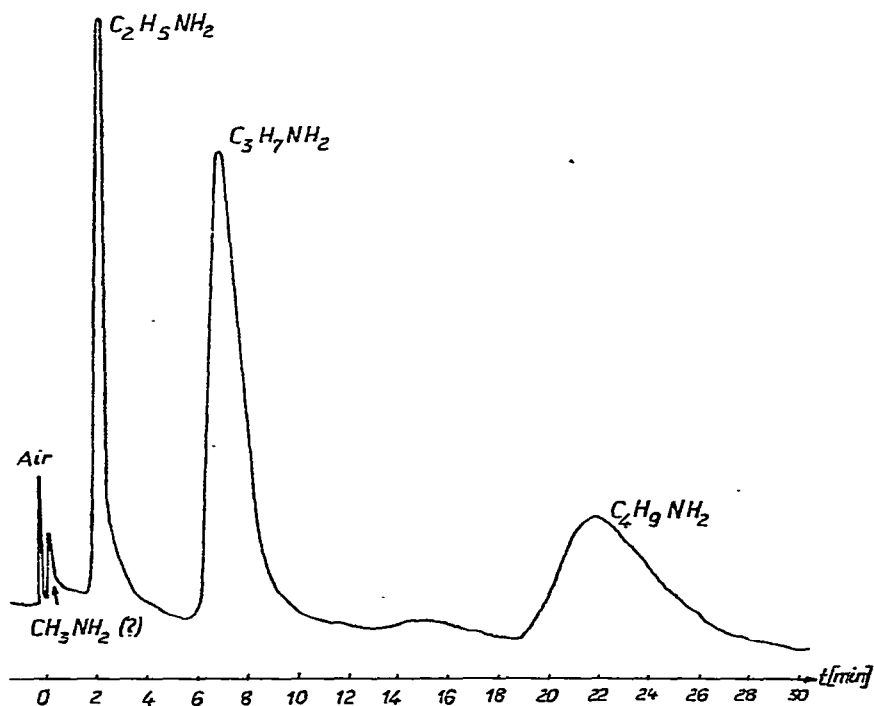

Fig. 6. Determination of amines. Column: 2 m × 4 mm I.D., glass, Chromosorb 103. Carrier gas: nitrogen–oxygen (95:5). Temperatures: column, 120°C; detector, 50°C. Concentration of trifluoro-acetic acid: 100 ppm. Sample size: 100 μl air with $7 \cdot 10^{-8}$ g $C_2H_5NH_2$, $5 \cdot 10^{-7}$ g $C_3H_7NH_2$, $5 \cdot 10^{-7}$ g $C_4H_9NH_2$.

CONCLUSIONS

These studies show that a sensitive and selective detection of halocarbons, SO_2, NO_2 and amines with the AID is possible. The detection limits in the most favourable cases (detection of halocarbons with reaction oven and subsequent amine reaction) are 10 ppb, and in other cases (detection of halocarbons with reaction oven, detection of SO_2 and NO_2) lie between 100 ppb and 500 ppb. The dynamic range amounts to 10^2.

Using ³H sources with a higher saturation current than available in our arrangement (10^{-9} A), and using space charge effects[14–16], an improvement of sensitivity and detection limit can be expected. Detection limits of 1–10 ppb for all the applications seem to be possible.

Difficulties do occur, especially in the detection of amines, owing to the necessity to keep the detector temperature below 60°C.

The greatest advantage of the AID is the very high selectivity in each mode of operation. A great number of applications are possible owing to the various methods for the formation of aerosols.

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