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APPLICATION OF PYROLYSIS–GAS CHROMATOGRAPHY WITH A MULTIDETECTOR TO AEROSOL ANALYSIS

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SUMMARY

A technique for aerosol detection and identification by pyrolysis–gas chromatography is presented. The aerosols were collected on powdered materials packed in a filtering tube and then pyrolyzed by heating the tube. A sufficiently complete trapping of aerosols was provided by crushed silica glass; both aerosols and vapours were readily collected by adsorbents, such as molecular sieves. Identification was carried out using a multidetector with three recording channels.

INTRODUCTION

Gas chromatography (GC) is widely used for determination of atmospheric pollutants, such as the vapours from various compounds and aerosols. Aerosols are usually adsorbed by filters[1], and when substances are present as vapours and aerosols, the filters are combined with adsorbents. In order to extract aerosols from filters, organic solvents are used[2].

A variety of aerosols have complex compositions. Such is the case for dusts from cotton, wool, protein–vitamin concentrate, flour, etc., which are difficult to extract from the filter. In the present work, they were detected by pyrolysis–GC. For simplicity, pyrolysis was carried out directly on the filter, without washing out the collected aerosols. For this purpose the aerosols were precipitated on materials having high thermal stabilities. The technique and apparatus developed are applicable to substances present as aerosols and as vapours, *e.g.*, pesticides. To make the pyrograms more informative, they were recorded using a dual-flame multidetector.

EXPERIMENTAL

The GC apparatus is shown in Fig. 1. The sampler (1) is a rotary device with six U-shaped filtering tubes (7–12), 4 mm I.D., mounted on a rotating lower disk (6). A valve (2) provides the connection of each of the tubes to a chromatographic column (16). A multidetector (17) and recording unit (23) with a double-channel recorder serve for recording chromatograms. The filtering tubes are displaced by drive 5, the valve by drive 3. Inside each silica glass filtering tube there is a hollow stainless-steel tube (13) closed with a gauze (14), 0.1-mm mesh, to keep the filtering bed within the
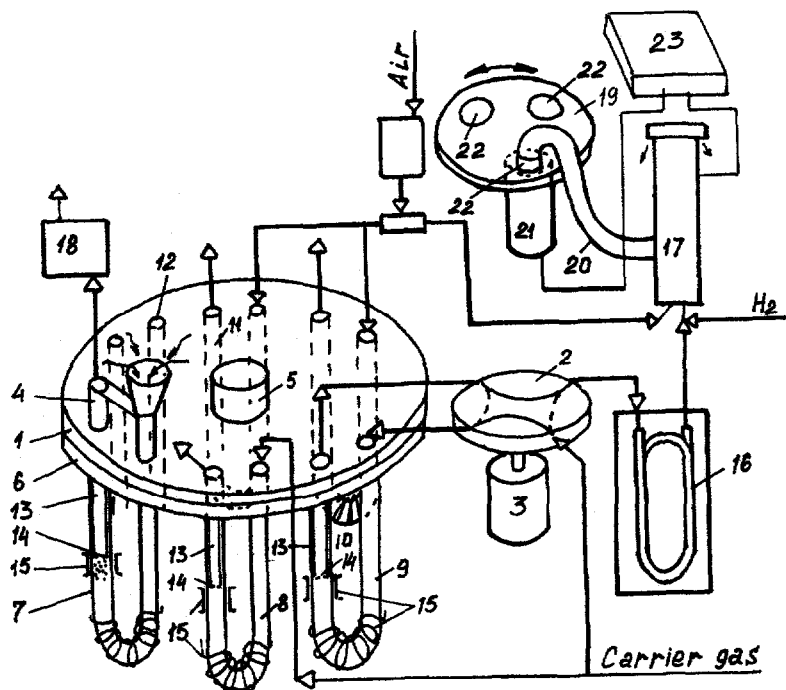
Fig. 1. The experimental apparatus: 1 = sampler; 2 = valve; 3 = valve electric drive; 4 = valve; 5 = sampler electric drive; 6 = rotating disk; 7–12 = filtering tubes; 13 = discharge tube; 14 = gauze; 15 = heater; 16 = chromatographic column with oven; 17 = multidetector; 18 = YK-40/2 compressor; 19 = light filter changing device; 20 = light guide; 21 = photomultiplier; 22 = light filters; 23 = recorder.

zone of an auxiliary external heater (15). A second heater, the main one, is mounted in the bent part of each glass tube. Both heaters are made of nichrome wire, 0.3 mm in diameter, and connected in series, their total resistance being 7 Ω. The heaters are powered by a 27-V supply. Each of the filtering tubes is packed with the same amount of a filtering powder (0.25–0.5 mm), and can be displaced after a definite time (3, 5, 10 or 20 min) to a new position where an analysis step is performed.

In the first step, the air to be analyzed was pumped, through a valve (4), into a filtering tube by means of a type YK-40/2 compressor. In this case the filtering powder is lifted toward the gauze (14) to enable aerosol precipitation thereupon. In the second step, a carrier gas was passed through tube 8, with the heaters being "on" or "off". In the third step, static pyrolysis in an inert atmosphere was conducted at 700°C for a prescribed time in tube 9 sealed with the valve (2). When tube 9 is connected, by valve 2, to the carrier-gas stream, the pyrolysis products are passed into the chromatographic column. In the fourth and fifth steps, the filtering powder in tubes 10, 11 and their walls were cleansed of the tarry residues of pyrolysis by pumping purified air through the tubes, with to 700°C. In the sixth step, tube 12 was cooled. Pyrolysis products were separated at 110°C on a 1 m × 3 mm I.D. column packed with Polysorb-I; the flow-rate of the carrier gas (nitrogen) was 60 ml/min.

Pyrograms were recorded using a dual-flame multidetector which combines the properties of three detectors: flame ionization, surface ionization and flame photo-
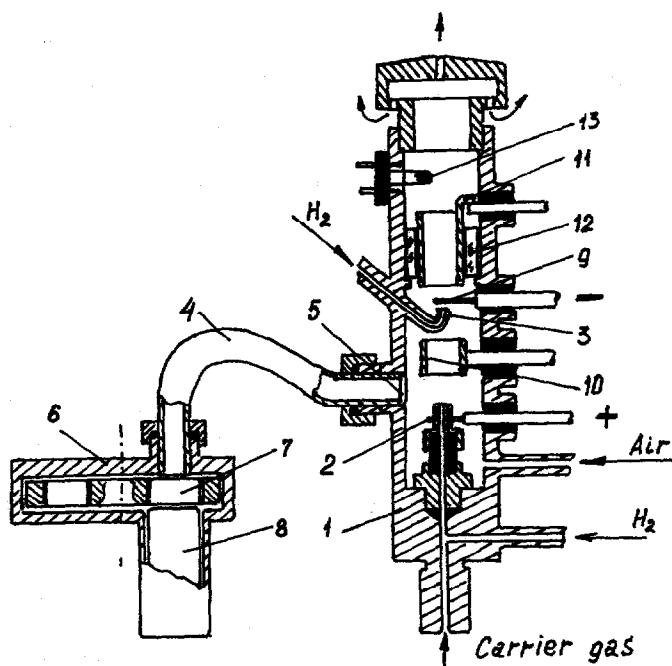
Fig. 2. Detector: 1 = casing; 2, 3 = lower and upper burners; 4 = light guide; 5 = transparent quartz (silica) glass disk; 6 = turret; 7 = light filters; 8 = photomultiplier; 9 = surface ionization electrode; 10, 11 = electrodes; 12 = quartz (silica) glass bushing; 13 = spiral for flame initiation.

metric. This detector is depicted in Fig. 2. In the lower burner flame zone there is a light guide (4) protected with a disk (5) made of transparent silica glass. The other end of the light guide is connected to a turret (6) with four movable interference filters (7) for different transmitted wavelengths. Each of the filters can be mounted between the light guide and a photomultiplier (8). A metal surface ionization electrode (9) is positioned above the upper burner (3). Signals from the lower and upper burners are carried to electrodes 10 and 11, respectively. The lower burner is at +300 V, electrode 9 at −300 V. The burners are made of stainless steel. The surface ionization electrode is an L-shaped wire, 0.4 mm diameter, part of it being directly in the burner flame.

The main dimensions of the detector units are as follows: diameter of the cell lower part, 7 mm; cell height before the joint, 50 mm, after the joint, 45 mm; first burner, standard one from a Tsvet-104 chromatograph; distance between the lower burner and electrode, 6 mm; diameter, length and thickness of the lower electrode, 5, 5 and 0.3–0.4 mm; distance from the upper burner to the lower electrode, 4–5 mm; inner diameter of the upper burner, 0.5 mm; distance between the upper burner and the surface ionization electrode, 1.0–1.5 mm; thickness of the surface ionization electrode, 0.4 mm; distance between the surface ionization electrode and the upper electrode, 1.5 mm; diameter and length of the upper electrode, 5 and 10 mm; light-guide axis, 2.5 mm from the burner end; light-guide diameter, 5 mm.

DISCUSSION

The degree of precipitation of aerosols depends on the nature of the filtering bed. The following filtering materials were investigated (particle dimensions 0.25–0.5 mm): silica glass; porcelain; molecular sieves; Chesasorb AW. Aerosols of metaphos, chlorophos, cotton, wool and protein–vitamin concentrate (PVC) were analyzed.

Crushed quartz glass proved to be the best material for analysis of the solid aerosols of cotton, wool and PVC with particle dimensions of 5–20 μm. A packed bed of 10 mm in height was capable of trapping aerosols with an efficiency of more than 95% at air flow-rates of 3–5 l/min. Powdered porcelain, molecular sieves and Chesasorb were difficult to cleanse of the tarry pyrolysis products.

When substances are present both as aerosols and as vapours, it is better to employ materials with a higher adsorptivity. Thus, for example, the adsorption of chlorophos and methaphos was 90- and 30-fold higher, respectively, on Chesasorb and molecular sieves than on a quartz glass powder. However, these materials are not strong enough and difficult to cleanse of tarry residues and ash, making them unsuitable for repeated tests. Quartz glass powder filters are stronger and are easy to clean.

As a rule, non-volatile or poorly volatile compounds are identified in pyrolysis GC by their peak height or peak area ratios. In static pyrolysis, the number of peaks on a chromatogram is not large. That is why the successful determination of the chemical composition of an aerosol requires additional information. The successive pyrolysis of the products precipitated on the filter at ambient temperature and then at an elevated temperature can yield information on the volatility of the aerosol. Volatiles are retained on sorbents more readily than on quartz (silica) glass powder. Hence, a comparison of the intensity of the detector signals for two successive analyses can give information on the properties of the aerosol constituents.

To determine the chemical composition of the aerosols by pyrolysis, a multidetector was used. The characteristics of the surface ionization and flame photometry channels were found in preliminary experiments. The surface ionization noise was 10^{-12} A, with helium as the carrier gas and at the optimum hydrogen and air flow-rates. The limit of detection was $8.2 \cdot 10^{-10}$ g/s for acetonitrile and methylene chloride, corresponding to a minimum detectable amount of acetonitrile of $2 \cdot 10^{-8}$ g. The ionization efficiency was equal to $1.25 \cdot 10^{-7}$ A/mg $\cdot$ s.

Surface ionization is determined by the metal electrode temperature and is dependent on the flow-rates of hydrogen and air. The optimum hydrogen flow-rate was 35–40 ml/min; at flow-rates greater than 40 ml/min the detector noise increased and the sensitivity became poorer. With increasing flow-rate of air a higher sensitivity was observed; however, at flow-rates over 400 ml/min the detector noise increased. The optimum flow-rate of air was 350 ml/min.

An increase in the carrier-gas (helium) flow-rate from 40 to 70 ml/min resulted in a decreased limit of detection. The optimum flow-rate for the surface ionization proved to be 55–60 ml/min. At flow-rates below 40 ml/min a considerable increase in noise and some peak tailing were observed. The reduction in noise, peak tailing and limit of detection with increasing carrier gas flow-rate is connected with a lower degree of mixing of the pyrolysis products after the lower burner, and with their shorter residence time between the electrodes.

Stainless steel, nickel and platinum were used as materials for the surface ionization electrode. The detector sensitivity was highest when a new electrode was fitted. After several hours of electrode operation in the hydrogen flame the detector sensitivity and noise decreased and stabilized, being practically invariable for subsequent operation. Thin nickel and nichrome electrodes lost their ionization properties most rapidly, particularly when compounds with high sulphur contents were analyzed. In this case the stabilized sensitivity of the detector was low. Platinum appeared to be the best material for the surface ionization electrode: even at high concentrations of substances, it yielded consistent results over a long period of operation.

The surface ionization mechanism has not yet been elucidated in detail. In the detector described, the heated surface is at a negative potential, and the ions of alkali metals emitted by the surface cannot take part in the process. It is most likely that the pyrolysis products are chemisorbed on the heated metal surface as radicals with a high electron affinity. The negative ions produced on the surface are then desorbed, giving rise to an electric current. Not only atoms and compounds of halogens possess a high electron affinity (Cl, 3.61 eV; CCl_4, 2.12 eV), but also a number of nitrogen- and phosphorus-containing radicals and compounds, such as CN (3.82 eV), NO_2 (3.1 eV) and PO (1.6 eV), which are probably formed in the flame and on the surface.

The minimum detectable amount (hydrogen sulphide) for the flame photometric unit of the detector is $3 \cdot 10^{-9}$ g with a 395-nm light filter and at a photomultiplier voltage of 700 V, *i.e.*, at a comparable level with detectors described in the
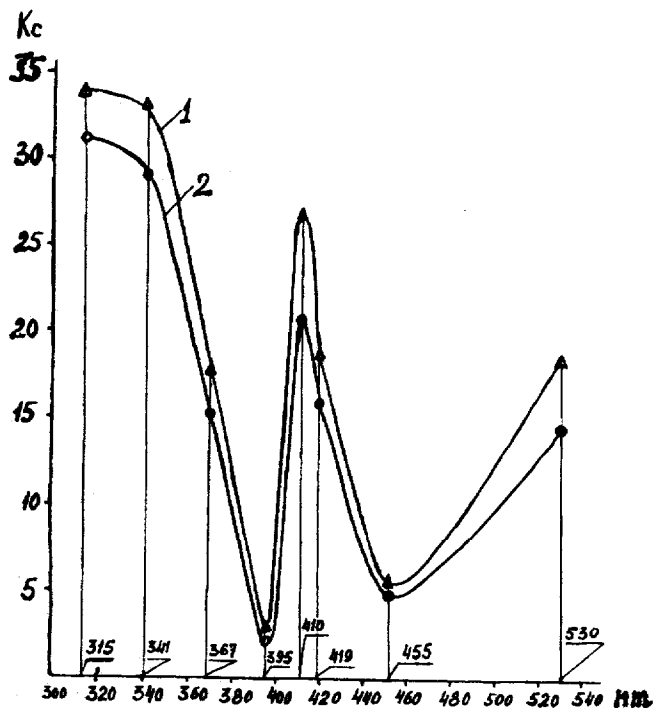

Fig. 3. Selectivity with respect to acetonitrile as a function of filter wavelength. Curves: 1, helium; 2, nitrogen as the carrier gas.

literature. However, its sensitivity with respect to hydrocarbons is tens of thousands times lower than that of a flame ionization detector. For sulphur- and phosphorus-containing compounds, filters with wavelengths of 395 and 526 nm are used, respectively. At such wavelengths, nitrogen-containing compounds are, also recorded.

The selectivity of the photometric detector with respect to nitrogen-containing compounds was studied in comparison with alcohols at 315, 341, 367, 395, 410, 419, 455 and 530 nm. The selectivity, K_s, was calculated as the peak area ratio for acetonitrile and propanol in a 1:1 mixture. Fig. 3 presents K_s as a function of wavelength, with helium and nitrogen as the carrier gas. The maximum selectivity is observed at 315 and 341 nm, the minimum at 395 and 455 nm. At 410 nm the selectivity is also high enough, and the minimum detectable amount of acetonitrile is a factor of 2–3 lower than at 315 and 341 nm. Thus, the use of a 410-nm filter enables one to determine, with high selectivity and sensitivity, nitrogen-containing compounds in mixtures with a large amount of hydrocarbons. Additional recording of the flame emission at 395 nm makes it possible to identify simultaneously sulphur- and nitrogen--containing compounds. Emission from nitrogen- and sulphur-containing compounds in the upper flame is a factor of 10 less than in the lower flame, but the reliability of identification may be higher due to the fact that the signal in the upper flame from compounds not containing these elements is many times less than in the
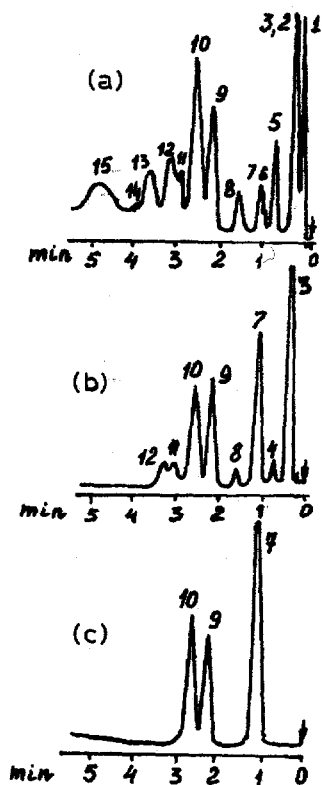

Fig. 4. Pyrograms of a protein–vitamin concentrate, recorded by flame ionization (a), flame photometric (b) and surface ionization (c) detection.

lower flame. Examples of the identification of compounds present in pyrolysis products by use of the multidetector are given below.

Fig. 4 presents the pyrograms of the protein–vitamin concentrate. On chromatogram a, which corresponds to flame ionization detection, nitrogen-containing compounds are recorded. With the aid of retention data they were identified as methylethylenimine (7), acetonitrile (9) and methyl isocyanide (10). On chromatogram b, corresponding to flame photometric detection at 395 nm, hydrogen sulphide (3) and an unidentified sulphur-containing compound (4) are recorded, as well as some hydrocarbons whose peaks are weaker than on chromatogram a. The photometric unit provides a sufficiently good recording of nitrogen-containing compounds even at 395 nm. On the chromatogram recorded from the upper flame (c) there were only peaks 7, 9 and 10.

The ability of the multidetector to detect nitrogen-, phosphorus- and sulphur-containing compounds in the presence of large amounts of hydrocarbons facilitates aerosol identification. The identification is more reliable for compounds which differ in their chemical composition from natural aerosols (pollen, earth dust, etc.). For example, nitrogen-, phosphorus-, sulphur-containing pesticides and wool particles can be identified in the presence of natural aerosols more easily than PVC dust or flour.

Phosphorus-containing aerosols (chlorophos, methaphos) can be distinguished from dust particles containing nitrogen (PVC, pollen) or sulphur (wool dust). Fig. 5 presents pyrograms of aerosols of methaphos, birch pollen and wool dust recorded by the multidetector. The upper chromatograms were recorded by flame ionization, the lower ones by flame photometry at 528, 410 and 395 nm, respectively. Intense
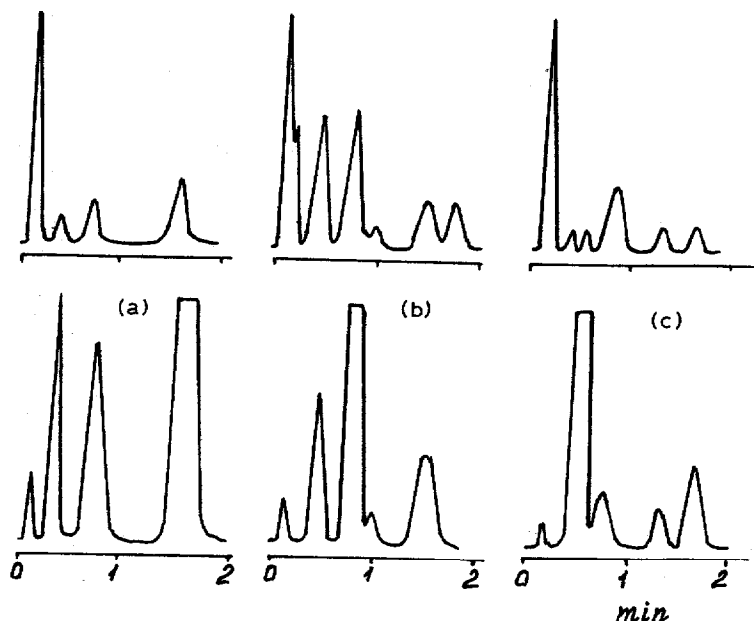

Fig. 5. Pyrograms of methaphos (a), birch pollen (b), and wool dust (c); recorded by the flame ionization detector, (upper) and by the flame photometric detector (lower) with light filters of wavelengths 528 (a), 410 (b) and 395 nm (c).

peaks of phosphorus-containing compounds can be seen on the chromatogram for methapos recorded by flame photometry. Nitrogen-containing compounds can be observed on the chromatogram for birch pollen, and sulphur-containing compounds on the chromatogram for wool dust.

Aerosols of identical elemental composition, say, PVC and pollen, are more difficult to distinguish. In some cases this can be achieved only by calculating the area ratios for peaks recorded by two or three channels of the detector.

The information provided by pyrograms showing a small number of peaks is insufficient for similar compounds to be identified. However, the high intensity of the peaks and the short retention times of volatiles enable rapid detection of aerosols of different types. For quantitative analysis of an aerosol, the representative peaks (or one of them) are chosen and an absolute calibration carried out by pyrolyzing weighed amounts of a material.

REFERENCES

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