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STEAM GAS–SOLID CHROMATOGRAPHY: A FLEXIBLE SEPARATION TECHNIQUE*

C. L. GUILLEMIN* and J. L. MILLET
Rhône-Poulenc Recherches, 12–14 rue des Gardinoux, F-93308 Aubervilliers Cedex (France)
and
E. HAMON
5 rue des Marais, 95210 Saint-Gratien (France)
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SUMMARY

The nature and specific surface area of the adsorbents and the composite mobile phase are the main parameters that make steam gas–solid chromatography a flexible separation technique. Some examples are presented that indicate the effectiveness of the steam generator and the potential of the technique for the direct analysis of aqueous samples.

INTRODUCTION

Despite the choice of modern chromatographic techniques now available, some analytical problems in industry remain unsatisfactorily resolved, mainly because of sample conditioning difficulties. For instance, with aqueous samples, complex sample conditioning systems involving physical or chemical treatments, such as extraction, concentration or reaction, are often set up in order to make the gas or liquid sample compatible with the requirements of the chromatographic process.

For the analysis of aqueous mixtures containing more or less volatile organic materials, steam gas chromatography (steam GC) could be an appropriate solution because as the mobile phase and the sample have the same matrix, water, part or whole of the sampling treatment can be avoided.

In a previous paper, Guillemin *et al.*[1] showed that steam GC has the greatest potential when performed on the one hand as steam-modified GC using adsorbents of variable specific surface area, and on the other by using an adjustable composite mobile phase of steam plus carrier gas instead of steam alone, unlike Nanoka[2–4], who used steam as the mobile phase, and more recently other users[5–7].

This paper describes the definitive techniques adopted and the use of different

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parameters to make this technique more flexible, efficient and reliable either in the laboratory or in on-line process GC.

INSTRUMENTATION

For feeding a gas chromatograph with a composite mobile phase (steam + nitrogen, helium or hydrogen), two solutions are proposed: (a) an inexpensive solution[1], which consists in continuously feeding both a controlled flow of water to be vaporized and carrier gas into a vaporizing mixing chamber before entering the chromatographic injection port (Fig. 1B) and (b) a more expensive, but more reliable, method in which dry carrier gas is bubbled into a temperature-controlled water tank before entering into the injection system (Fig. 1A).

The first system (Fig. 1B) consists of a pressurized pumping reservoir set outside the chromatographic oven and maintained at room temperature, and has already been described in detail[1]. Nevertheless, some comments will be made here to give a

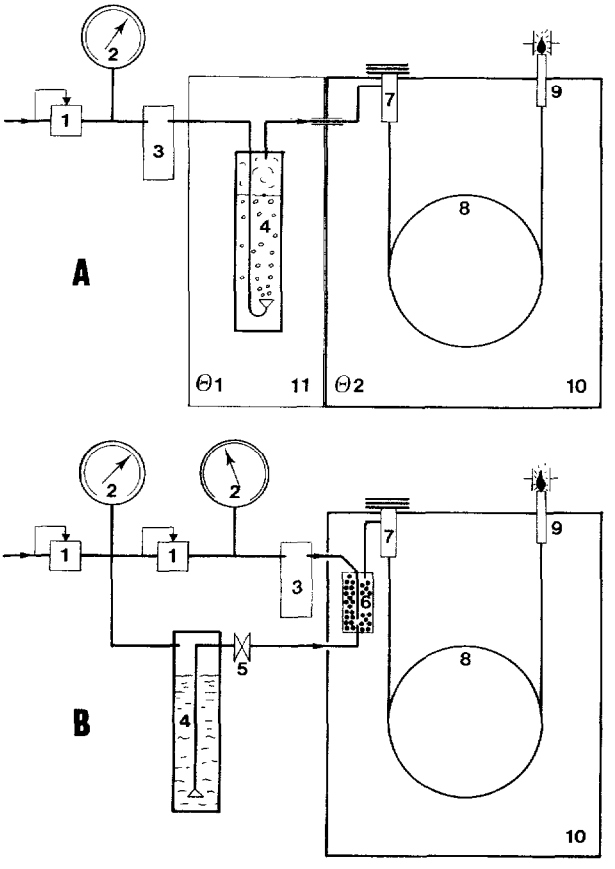

Fig. 1. Schematic diagrams of steam generators. (A) New system; (B) old system. 1 = Pressure regulator; 2 = pressure gauge; 3 = guard pot; 4 = water reservoir; 5 = metering needle valve; 6 = heat exchanger; 7 = injection port; 8 = column; 9 = flame-ionization detector; 10 = chromatographic oven; 11 = water reservoir oven.

better understanding of the difficulties encountered. The main problem lies in finding a metering valve fine enough to feed a constant flow of water of a few (10–30) microlitres per minute for a long period of time (1 week minimum). By adding a capillary tube (10 m × 0.25 mm I.D.) downstream of the valve some improvement may be expected, but this system has been given up in favour of the second one, which fits more closely the criteria of industrial instrumentation.

In the second system (Fig. 1A), constancy of the composite mobile phase is obtained by passing through a controlled-temperature reservoir, filled with a liquid such as water, carrier gas (nitrogen, helium or hydrogen) at a given flow-rate and making it bubble into the heated liquid. Other liquids can be also used, such as carbon disulphide or ammonia solution depending on the practical application.

To avoid any drawbacks due to possible condensation of steam between the exit of the controlled-temperature reservoir and the detector, some precautions are essential (a) the reservoir oven must be close to the column thermostat and the tube leading the composite mobile phase to the injection port must be heated at a temperature higher than that of the reservoir; and (b) the working temperature of the column must always be kept slightly higher than that of the reservoir.

If condensation occurs, it causes detector instability and baseline disturbances when pushed by the mobile phase into a hot part of the circuit, where it vaporizes again. Likewise, to avoid a noisy baseline, the plunger in the water reservoir must be ended with a 10–20 μm frit.

A flame-ionization detector is the most commonly used detector in steam GC and the hydrogen flow-rate is slightly increased with respect to normal operation in order to keep the flame temperature high enough to allow the ionization phenomenon to take place. On average, for a composite mobile phase of 3 l/h (50 ml/min) the hydrogen flow-rate will be set at 5 l/h (80 ml/min) and the air flow-rate within the range 10–20 l/h (170–330 ml/min). On the other hand, it is advisable to remove the flow controller which is generally present in any chromatographic pneumatic circuit because it is responsible for baseline disturbances with large sample injections, for instance when detecting trace amounts of organic materials in water (see the section on applications).

The saturated vapour pressure at a fixed temperature allows one to determine the correct composition of the mobile phase: knowing the pressure before and after setting up the temperature of the reservoir, the relative volumetric composition can be calculated as follows:

$$P_3 - P_1 = P_2 \tag{1}$$

$$P_2/P_3 = \%\ \text{steam}$$

$$P_1/P_3 = \%\ \text{carrier gas}$$

where P_1 is the carrier gas pressure before heating the reservoir, and is checked on pressure gauge G_1, P_2 is the pressure of the steam at a fixed temperature and P_3 is the total pressure after heating the reservoir, checked on pressure gauge G_1. The total mobile phase and steam flow-rates can be easily calculated with sufficient accuracy from the carrier gas flow-rate and pressures P_1, P_2 and P_3.

An interesting feature is the possibility of programming the reservoir temperature to vary the mobile phase composition as a function of time, while the column temperature remains constant, in order to reduce the retention times and improve the shape of the most retained peaks.

OPTIMIZATION OF STEAM GAS CHROMATOGRAPHIC PERFORMANCE

Several parameters govern the performance expressed in terms of selectivity and analysis time of the steam GC technique: the nature of the adsorbent, the specific surface area of the adsorbent, the relative pressure of steam in the mobile phase and the column temperature.

Nature of the adsorbent

It is obvious that steam GC may be carried out with any adsorbent, *e.g.*, silica, pyrocarbon–silica (prepared by H. Colin, Ecole Polytechnique, Palaiseau, France), alumina, active carbon or porous polymers. The process involved in steam GC, being modified gas–solid chromatography, implies an active role for the adsorbent itself in

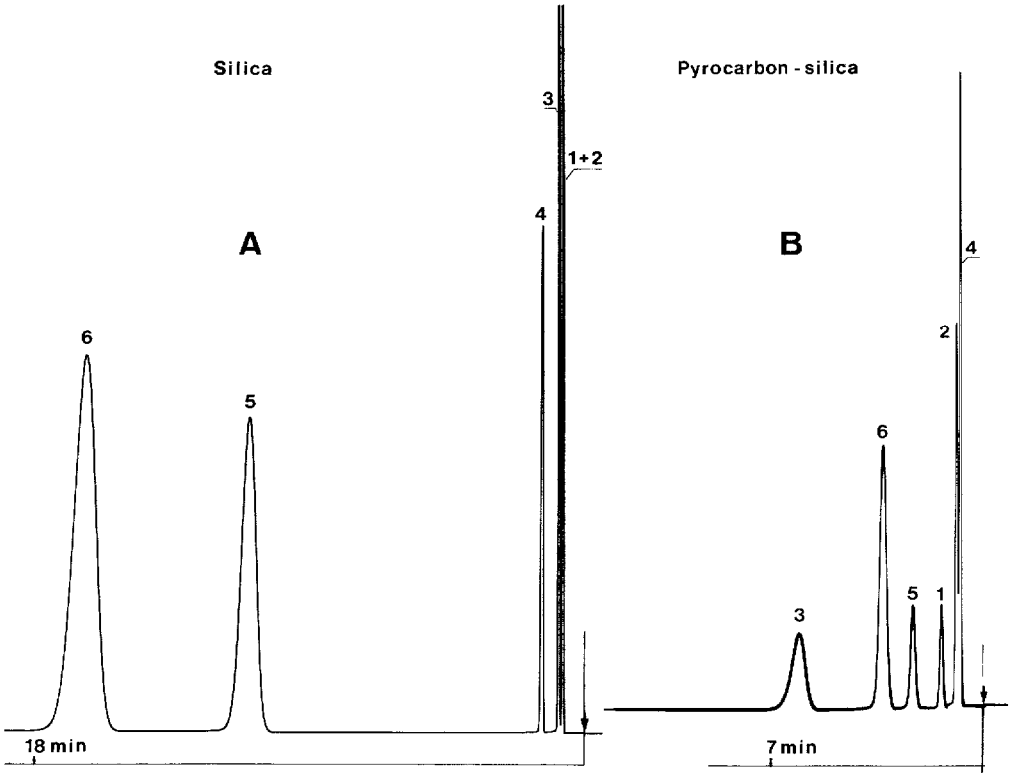

Fig. 2. Separation of a test mixture on silica and pyrocarbon silica by steam GC. (A) Silica: column, 2 m × 4 mm I.D. Spherosil, 32 m^2/g, d_p = 150–200) μm; column temperature, 150°C; flow-rate, 2.9 l/h (N_2–H_2O, 52:48). (B) Pyrocarbon silica (prepared by H. Colin, Ecole Polytechnique, Palaiseau, France): column, 1 m × 4 mm I.D., pyrocarbon Spherosil, 50 m^2/g, d_p = 150–200 μm; column temperature, 150°C; flow-rate, 3.06 l/h (N_2–H_2O, 56:14). Peaks: 1 = 3-methylpentane; 2 = cyclohexane; 3 = heptane; 4 = 1,2-dichlorethane; 5 = acetone; 6 = methyl ethyl ketone.

the separation process, as discussed previously[8]. A given mixture may give different patterns of separation according to the nature of the adsorbent and the specific interactions developed. Fig. 2A and B illustrate a separation carried out by steam GC, first on silica, with the elution order 3-methylpentane, cyclohexane, heptane, 1,2-dichlorethane, acetone and methyl ethyl ketone, and second on pyrocarbon silica, with a different elution order, 1,2-dichlorethane, cyclohexane, 3-methylpentane, acetone, methyl ethyl ketone and heptane.

It should be noted that on silica, the greater the polarity of the molecules the longer is the retention time, whereas on pyrocarbon–silica, the elution order alters so that the oxygenated compounds precede the hydrocarbons.

Influence of the specific surface area of the adsorbent[8]

The specific surface area of the support is related to the retention time (t_R) by the well known relationship

$$t_R = L/u\,[1 + K_p\,(Spd_f/V_M)]$$

where L is the column length, u the linear velocity of the mobile phase, K_p the distribution coefficient, S the specific surface area of the adsorbent, p the weight of the adsorbent in the column, d_f the film thickness of the liquid stationary phase and V_M the mobile phase volume.

As the process behaviour of steam GC is similar to modified gas–solid chromatography, the distribution coefficient K_p will depend on both the amount of adsorbed water on the surface of the adsorbent as stationary monolayers and the surface activity of the adsorbent itself. Under these conditions the distribution coefficient cumulates the contributions of the partition and adsorption coefficients. As already assumed by Snyder[9] and Kiselev[10] with silica, the surface activity varies with the specific surface area, so that the distribution coefficient, as an adsorption coefficient, will be strongly affected by this parameter, as shown in Fig. 3.

From Fig. 3 for the previous test mixture run at constant column temperature and mobile phase composition, the following practical observations may be noted: (a) the distribution coefficient, K, increases rapidly with increasing specific surface area of the support; (b) the separation of compounds with similar heats of adsorption requires the specific surface area of the adsorbent to be increased, for example 3-methylpentane and cyclohexane, the effective separation of which occurs on a 300 m^2/g silica; and (c) in contrast, high specific surface areas increase the retention times of compounds that have a strong affinity for the support, for example the oxygenated compounds acetone and methyl ethyl ketone.

Consequently, in isothermal operation with a constant mobile phase composition, steam GC appears to be a much more useful technique for the detailed separation of part of rather than the whole complex mixture, as is often required in on-line process GC.

Influence of the composition of the mobile phase

In addition to the previous parameters, the amount of adsorbed water on the surface of the adsorbent is a function of the relative pressure of steam in the mobile phase with respect to column pressure drop and temperature. At a given column

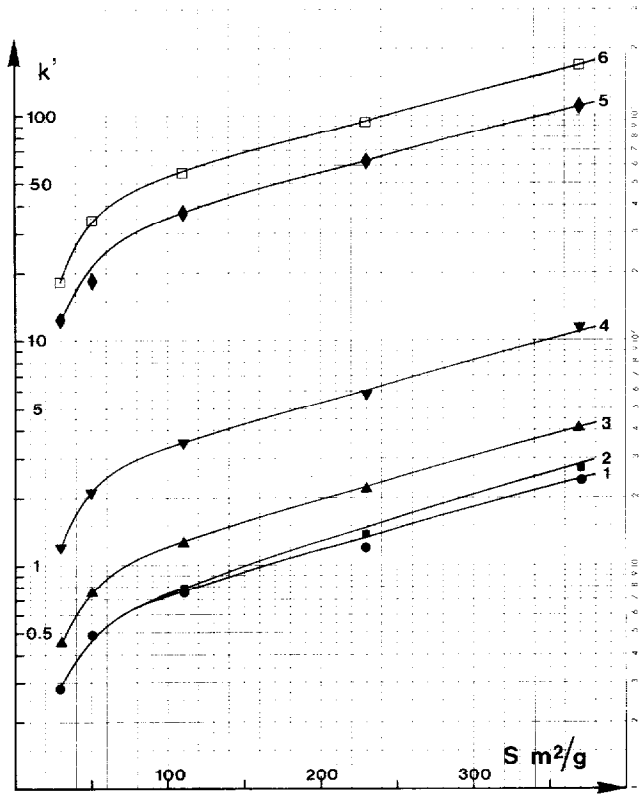

Fig. 3. Plots of *k' versus* specific surface area of the support. Column: 2 m × 4 mm I.D., silica Spherosil, 32, 53, 108, 230 and 367 m^2/g, d_p = 150–200 μm; column temperature, 115°C; flow-rate, 3 l/h (N_2–H_2O, 42:58). 1 = 3-Methylpentane; 2 = cyclohexane; 3 = heptane; 4 = 1,2-dichlorethane; 5 = acetone; 6 = methyl ethyl ketone.

temperature, increasing the relative pressure of steam reduces the activity of the adsorbent by blocking the active sites and increases the number of monolayers of adsorbed water and also the polarity of the mobile phase.

The influence of the mobile phase composition is illustrated in Fig. 4. The negative slopes show that the chromatographic process moves rapidly from adsorption when using a dry mobile phase to modified gas–solid chromatography as the relative pressure of steam increases. On the other hand, enriching the mobile phase with steam shortens the retention times.

However, the major difference between conventional modified gas–solid chromatography using low-vapour-pressure material as the stationary phase and steam GC, lies in the gradient of film thickness of adsorbed water, due to variation of the pressure drop along the column, giving a variable selectivity. This feature reveals an advantage for solutes with close *k'* values. Nevertheless, this effect can be easily controlled either by varying the amount of steam or by choosing a packing with a different specific surface area.

By analogy with liquid chromatography, it may be noticed that the polarity of the mobile phase in steam GC becomes adjustable.

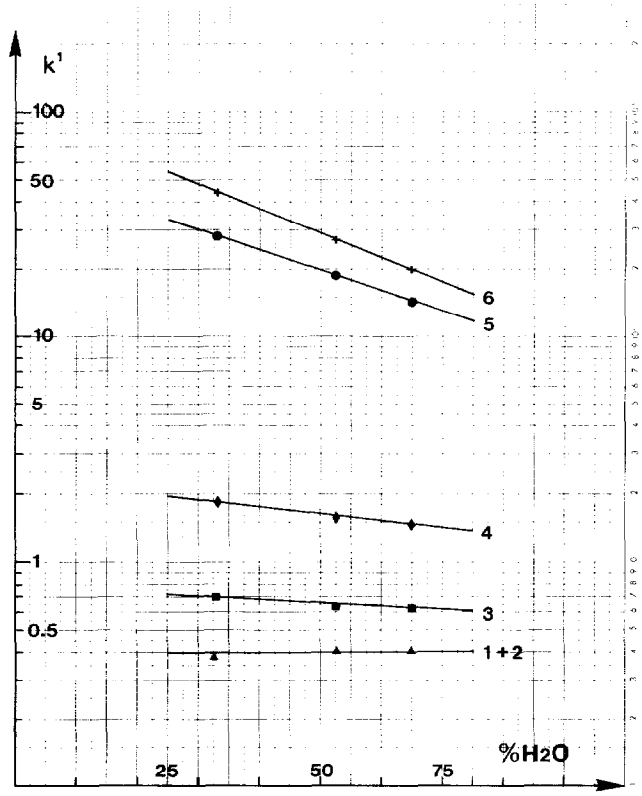

Fig. 4. Plots of k' *versus* percentage of steam in the mobile phase. Column: 2 m × 4 mm I.D., silica Spherosil, 32 m^2/g, d_p = 150–200 μm; column temperature, 115°C; flow-rate, 3 l/h (H_2O 33, 52 and 66%). 1 = 3-Methylpentane; 2 = cyclohexane; 3 = heptane; 4 = 1,2-dichlorethane; 5 = acetone; 6 = methyl ethyl ketone.

Influence of column temperature

Despite the gradient of water film thickness, as in any other chromatographic modes, the logarithm of the retention times may be plotted against the inverse of temperature in order to optimize a separation. For instance, in Fig. 5, the plots of log t_R for the test mixture components *versus* $1/T$, using pyrocarbon–silica and a constant mobile phase composition, show a surprising reversal for heptane with respect to the acetone and methyl ethyl ketone peaks.

Practical rules governing steam GC

The following general rules may be formulated for improved steam GC practice: (a) the higher the boiling point of organic materials, the lower should be the specific surface area of the adsorbent and the greater the steam content of the mobile phase; and (b) the greater the polarity of compounds, the lower should be the specific surface area of the adsorbent and the greater the steam content of the mobile phase.

According to Kiselev's classification of molecules[10], the following operating conditions may be recommended. For molecules of A and B groups (saturated, unsaturated and aromatic hydrocarbons, alcohols, ethers, ketones, etc.), choose an ad-

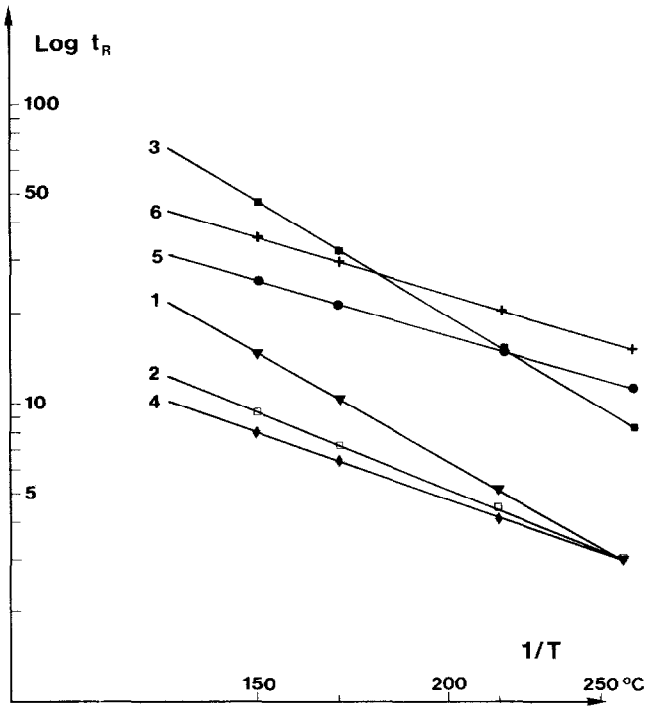

Fig. 5. Graphs of log t_R = f(1/T) for the test components. Column: 1 m × 4 mm I.D., pyrocarbon Spherosil 50 m^2/g, d_p = 150–200 μm; column temperature, 150, 170, 216 and 260°C; flow-rate, 3.06 l/h (N_2–H_2O, 56:44). 1 = 3-Methylpentane; 2 = cyclohexane; 3 = heptane, 4 = 1,2-dichlorethane; 5 = acetone; 6 = methyl ethyl ketone.

sorbent within the middle to high specific surface area range and a mobile phase composition of gas to steam within the range 75:25 to 50:50. For molecules of C and D groups (organometallic compounds, carbonyls, ester groups, polyglycols, amino alcohols, etc.), choose an adsorbent within the low to middle range, with a mobile phase composition of gas to steam within the range 50:50 to 25:75 or even greater.

EXAMPLES OF APPLICATION OF STEAM GC

Detectability in aqueous samples

To demonstrate the potential of the steam GC technique in the trace analysis of organic materials in water, the previous test mixture of cyclohexane, heptane, acetone and methyl ethyl ketone was dissolved in water at the parts per million level. The analysis was performed at 160°C on a silica packing of specific surface area 32 m^2/g with the detection conditions optimized for the flame-ionization detector (see caption of Fig. 6).

Under these conditions, on injecting 25 μl of aqueous mixture the limits of detection for the different components are cyclohexane and heptane 25 ppb* and acetone and methyl ethyl ketone 100 ppb.

* The American billion (10^9) is meant.

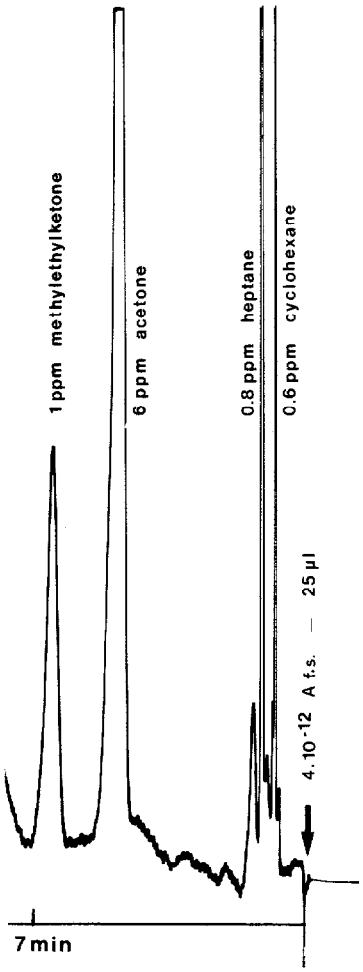

Fig. 6. Limits of detection of organic materials in aqueous samples. Column: 2 m × 4 mm I.D., silica Spherosil, 32 m^2/g, d_p = 150–200 µm; column temperature, 160°C; flow-rates, 3 l/h (N_2–H_2O, 35:65), H_2 12 l/h, air 9 l/h; injection, 25 µl.

One of the major advantages of steam GC is the possibility of injecting large volumes of aqueous samples without disturbing the baseline and avoiding any artefact at the beginning of the chromatogram. This feature is mainly due to the removal of the flow controller from the pneumatic circuit of the chromatograph. An excess of pressure corresponding to a large injection of sample into the column makes the flow controller react immediately to feed the column with a corresponding excess of carrier gas; by omitting the flow controller the process is reversed. The sudden rise in pressure slows the carrier gas, resulting in complete resorption of the large amount of the vaporized sample. Hence aqueous samples as large as 100, 200 or even 500 µl can be injected, with minimum baseline disturbance, and giving a considerable improvement in the limit of detection[1].

Impurities in acetic acid

An assessment of organic impurities in acetic acid was made by injecting the sample directly on to silica of specific surface area 360 m^2/g and using a composite mobile phase rich in steam (75%). As shown in Fig. 7, peaks of impurities elute very symetrically and the major acetic acid peak shows little peak tailing.

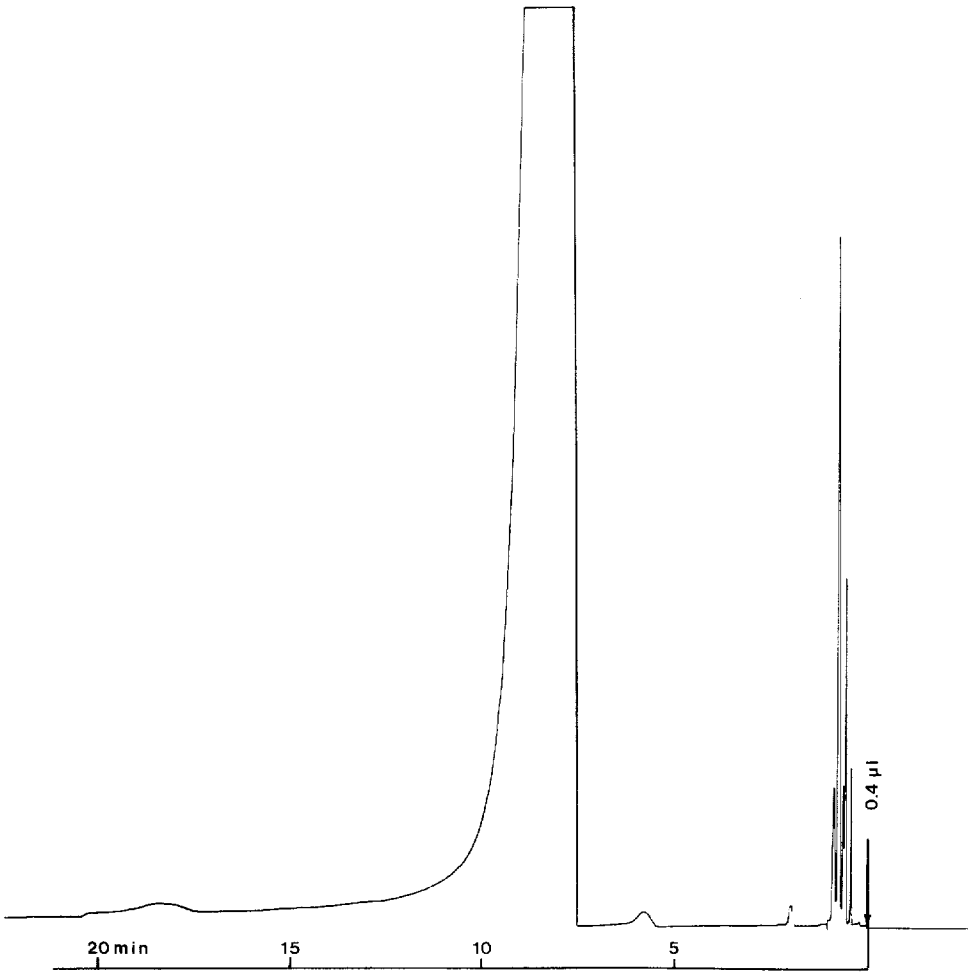

Fig. 7. Measurement of impurities in acetic acid. Column: 4 m × 4 mm I.D., silica Spherosil, 360 m^2/g, d_p = 100–200 µm; column temeprature, 130°C; flow-rates, 3 l/h (N_2–H_2O, 25:75), H_2 5 l/h, air 15 l/h; injection, 0.4 µl.

Separation of n-alkanols

In addition to the available adsorbents usable in steam GC, bonded phases are also useful in this technique, allowing new selectivities to be achieved. For instance, the separation of a mixture of C_1–C_7 *n*-alkanols was achieved on a C_{18} bonded silica of specific surface area 53 m^2/g (Fig. 8). The peaks are symmetrical and no appreciable decrease in resolution was observed after permanent operation for 1 week at temperatures up to 180°C.

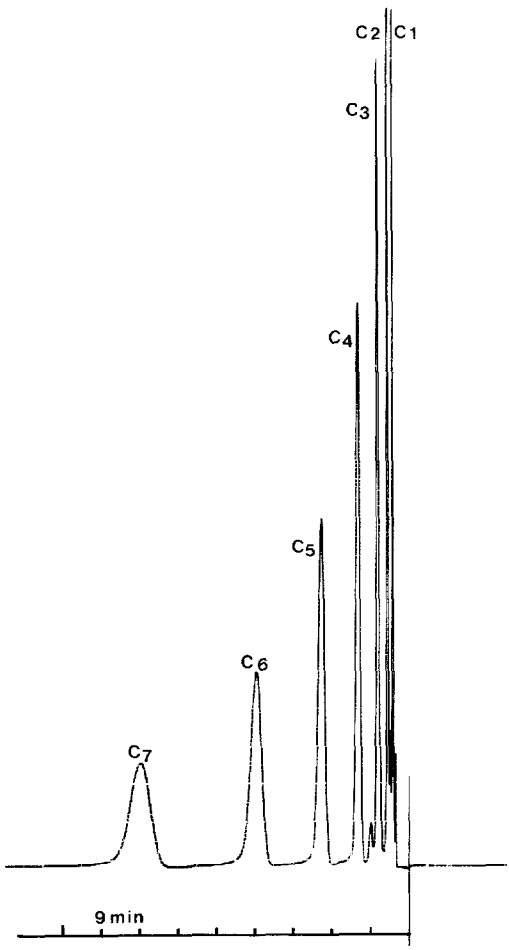

Fig. 8. Separation of C_1–C_7 *n*-alkanols on C_{18} silica. Column: 1 m × 4 mm I.D., C_{18}/Spherosil, 53 m^2/g, d_p = 150–200 μm; column temperature, 150°C; flow-rates, 3 l/h (N_2–H_2O, 64:36), H_2 5 l/h, air 16 l/h.

Separation of nitrogenous derivatives

A mixture of nitrogenous derivatives was successfully separated under severe conditions applied to reduce the activity of the chromatographic system, *viz.*, silica with a small specific surface area (15 m^2/g), a high column temperature (220°C) and a high steam content of the carrier gas (90%).

The choice of the column temperature (220°C) results in a compromise between obtaining a short elution time (higher temperature) and the amount of water as monolayers on the support (lower temperature) in order to obtain good resolution and symmetrical peaks for the solutes. Under these conditions, the separation was completed in a few minutes, with well shaped peaks (Fig. 9).

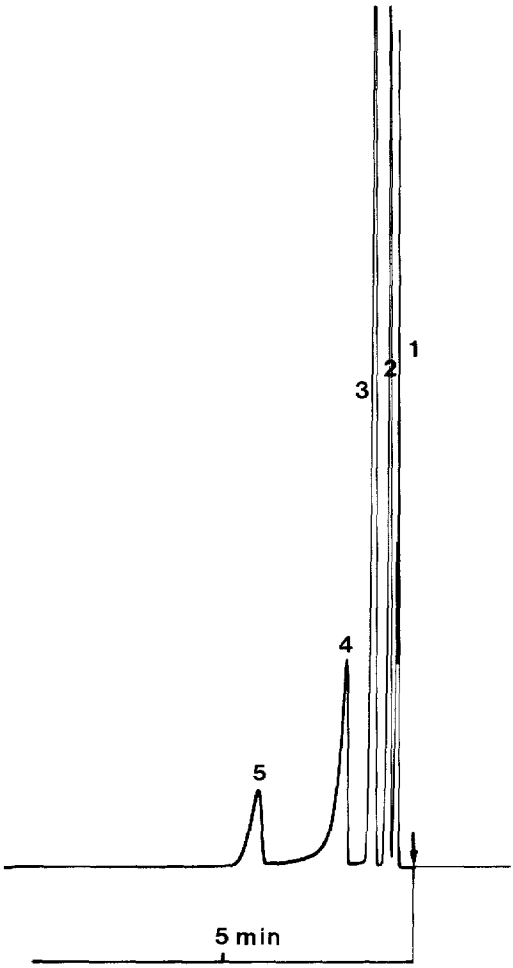

Fig. 9. Separation of nitrogenous derivatives. Column, 1 m × 4 mm I.D., silica Spherosil, 15 m^2/g, d_p = 100–150 μm; column temperature, 220°C; flow-rates, 3 l/h (N_2–H_2O, 10:90), H_2 5 l/h, air 16 l/h. Peaks: 1 = acetonitrile; 2 = nitrobenzene; 3 = pyridine; 4 = triethylamine; 5 = dimethylformamide.

CONCLUSION

Flexibility and detectability are the main characteristics of steam GC for the analysis of aqueous samples; the possibility of using any kind of adsorbents, bonded adsorbents, porous polymers, variable polarity of the mobile phase and large amounts of injected samples make this technique very powerful with respect to separation and detectability.

As a result of the recent technology adopted, steam GC may be considered as an adult technique to be used either in the laboratory or in on-line process GC for the routine control of difficult analytical problems.

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