GLASS CAPILLARY COLUMNS IN THE GAS CHROMATOGRAPHIC SEPARATION OF AROMATIC AMINES. I.

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SUMMARY

Preliminary results for the gas chromatographic analysis of aromatic amines on glass capillary columns are presented. The column is coated with a stationary phase of polyethylene glycol on a basic support, and it has been tested for polarity, adsorption and acidic properties. The separation number has been evaluated, and the measurement of film thickness is discussed. Splitless injection of aromatic amines is achieved with 2-butanone as the solvent.

INTRODUCTION

Aromatic amines (AA) are a group of chemical compounds consisting of aromatic molecules where at least one hydrogen atom is substituted with an amino group (primary AA). In turn, one or both of the hydrogen atoms in the amino group can be replaced by alkyl or aryl groups, thus giving secondary and tertiary AA, respectively. In this way, it is possible to synthesize a considerable number of compounds, and, as quoted by Scott[1], ". . . as the amines may react with other amines or other compounds the permutations and combinations are, in theory, infinite and in practice enormous".

The biological effects of AA vary from acute to chronic poisoning[1,2]; some AA can give rise to cancer of the bladder or exert irritant effects on the urinary tract, and many of them induce allergies.

Aromatic amines are used in several industrial processes, such as the production of dyestuffs and pigments, in the colouring of fur, as hair-dyes, in printing and painting, and as antioxidants in rubber.

The presence of AA is usually confirmed by thin-layer, high-performance liquid or gas chromatography (GC)[3–5]. Derivatization of the amines has been employed in GC to facilitate the analysis[6]. Such a step, however, introduces a possible source of sample contamination and necessitates a determination of synthesis yields in quantitative work.

It has been the aim of this work to develop a method for the direct GC of AA on glass capillary columns. Capillary columns were chosen because of their high re-

solving power and because the technique of their handling was already well established in our laboratory. Because of its selectivity and sensitivity for nitrogen-containing compounds, a nitrogen–phosphorus detector has been used; the results of this will be the subject of a future paper.

EXPERIMENTAL

The glass capillary column

Pyrex borosilicate-glass tubing (7 mm O.D. × *ca.* 2.6 mm I.D.) was drawn into a capillary on a horizontally working Hupe and Busch drawing machine, resulting in a 37-m column of 0.9 mm O.D. × 0.32 mm I.D., plus a buffer column of *ca.* 30% of the main column length. The temperature inside the oven was measured, without tubing, to be 1020° in the hottest zone. Water, acetone, and air were drawn through the tubing before it was drawn out .

The following procedure, leading to a capillary column of Carbowax 20M coated on a basic support, was carried out in accordance with the early barium carbonate method of Grob *et al.*; the method has been published in detail[7,8], and only the few deviations will be mentioned here.

As the column was to be used in the chromatography of AA, a basic support for the stationary phase was necessary for the elution of these basic compounds as symmetrical peaks. The 0.2% solution of Carbowax 20M originally used for deactivation of the barium carbonate crystals was therefore replaced by a similar solution modified with potassium hydroxide[9]: a 5% (w/v) solution of KOH in methanol was added to the 0.2% (w/v) solution of PEG 20M in dichloromethane to give a 0.1% (v/v) solution in the latter. No attempt was made to remove carbonates from the potassium hydroxide pellets used. A heat treatment at 280° completed the deactivation step.

All solutions were introduced in the capillary by nitrogen pressure and not by suction. This prevented evaporation of solvent from the liquid front (of the organic solutions), thus avoiding concentration here. The stationary phase was coated by using the mercury plug dynamic method. A modified version of the apparatus described by Schomburg and Husmann[10] for the introduction of coating solution and the mercury plug was used, thus ensuring that there was no air between the two liquids. Care was taken to prevent coating solution from entering the column after the mercury. When the plug left the column, excess of solvent was evaporated overnight with an increased nitrogen flow[11]. The coating parameters are given in Table I.

TABLE I

COATING PARAMETERS FOR THE MERCURY PLUG DYNAMIC METHOD

Stationary phase: Carbowax 20M
Solvent: Dichloromethane
Solution concentration: 12% (w/v), *i.e.*, 11.3% (v/v)
Solution density: 1.305 g/ml (ref. 12)
Solution viscosity: $1.226 \cdot 10^{-2}$ kg/m · sec (ref. 12)
Interfacial surface tension between Hg and CH_2Cl_2: $3.41 \cdot 10^{-1}$ N/m (ref. 12)
Internal diameter of the column: 0.32 mm
Linear coating velocity: 0.32 cm/sec, *i.e.*, 120 sec/coil
Length of the mercury plug: 4 cm

RESULTS AND DISCUSSION

Testing of the column

The column was tested for polarity, adsorption and acidic properties when freshly coated, after one night at the assumed max. temperature, 240° (we now·use the column up to 250°), and after a further 48 h at 240°; this last series of tests gave an indication of long-term stabilility. The test mixtures were the earlier ones proposed by Grob and Grob[13]. The conditioned column was finally evaluated for separation number.

As can be seen from Fig. 1, the ketone (at 80°, 5-nonanone is eluted together with *n*-tridecane) and the aromatic compound are chromatographed perfectly, with no tailing, on the freshly coated column. This is also true after 64 h at 240°. The ratio ar/16 (between the electronically integrated peak areas) only decreased by 1.5% during the conditioning. The alcohol, on the other hand, was adsorbed and eluted with tailing even in the preliminary testing. This effect grew worse with time and increasing temperature, the ratio ol/15 decreasing by almost 70%.
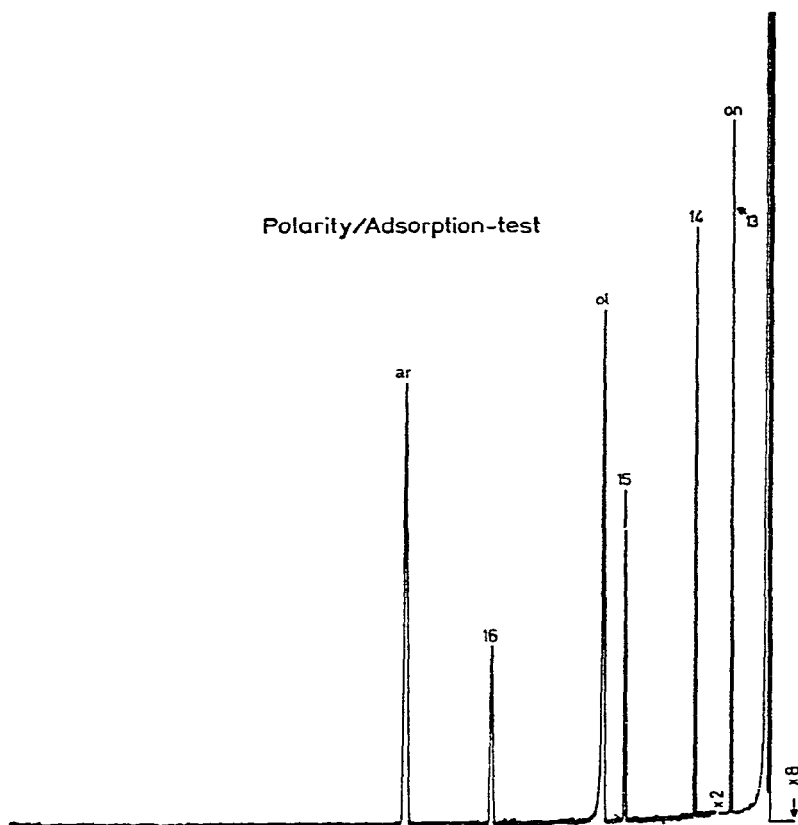
Polarity/Adsorption–test

Fig. 1. Polarity/adsorption test after 1 h at 150°. The ketone (on = 5-nonanone) and the aromatic compound (ar = naphthalene) show excellent non-tailing behaviour, while the alcohol (ol = 1-octanol) exhibits adsorptive influences. Split injection at 80°. Carrier gas, hydrogen 0.6 kp/cm^2; injector and detector temperature, 150°. Carlo Erba Fractovap 2350/FID chromatograph; Perkin-Elmer recorder 56, 2.5 mV full-scale. Chart speed, 5 mm/min. Solvent: dichloromethane.

The change in the Kováts retention index for the alcohol was, however, negligible. On the freshly coated column, the value of the index was 1521.3; after one night at the maximum temperature, it was 1522.4, and the value fell to 1521.4 after 64 h at 240°.

The results of the acidity tests are shown in Table II. The basic character of the column was maintained during conditioning and the ratio between the basic and the acidic compounds was constant. The acidity test also gave an indication that the column was suited to the chromatographic analysis of AA, as 2,6-dimethylaniline (DMA, itself an AA) eluted with perfect symmetry (see Fig. 2).

TABLE II

ACIDITY TEST OF THE POTASSIUM HYDROXIDE-MODIFIED CARBOWAX 20M COLUMN

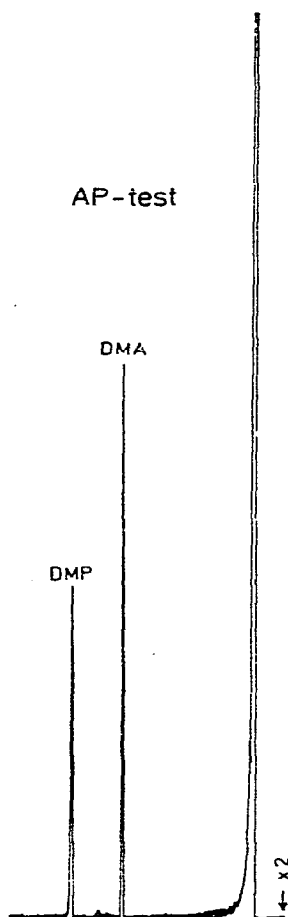| Ratio	1 h at 150°	16 h at 240°	64 h at 240°
DMA/DMP	1.20	1.25	1.19

Fig. 2. Acidity test after 1 h at 150° shows a basic column. The ratio of 2,6-dimethylaniline (DMA) to 2,6-dimethylphenol (DMP) is 1.20. Split injection at 120°. Other conditions as in Fig. 1. Solvent: n-hexane.

The separation number (TZ), measured between the n-C_{15} and n-C_{16} alkanes after 64 h at 240°, was 36 at 80° and 40 at 60°.

Measurement of the film thickness

As opposed to the static coating method, the film thickness resulting from a dynamic coating of the stationary phase cannot be measured directly from the solution concentration; several factors influence the result. Both Blomberg[11] and Alexander and Lipsky[12] have arrived at the conclusion that it is most practical to use the Fairbrother–Stubbs equation for prediction of the average film thickness, d_f, in dynamically coated capillary columns: thus,

$$d_f = \frac{c\,r}{200} \sqrt{\frac{u\,\eta}{\gamma}}$$

where c is the concentration (%, v/v) of the coating solution, η is its viscosity and γ its surface tension; r is the internal radius of the column, and u is the linear coating velocity.

When using a mercury plug in the dynamic method, Alexander and Lipsky[12] suggest replacement of γ by the interfacial surface tension between mercury and solvent. With this modification, the film thickness of PEG 20M in our column is 0.097 μm. This value is, however, still only approximate, because the equation does not take into consideration the length of the mercury plug. From the data of Alexander and Lipsky[12], the curve shown in Fig. 3 has been constructed. Even though those authors state that the film thickness ". . . is practically independent of the mercury plug length . . .", a decrease of almost 25% is observed when the plug length is increased from 5 to 25 cm. Since different authors tend to use different plug lengths, the fact is only mentioned in order that it should be remembered that reproducible
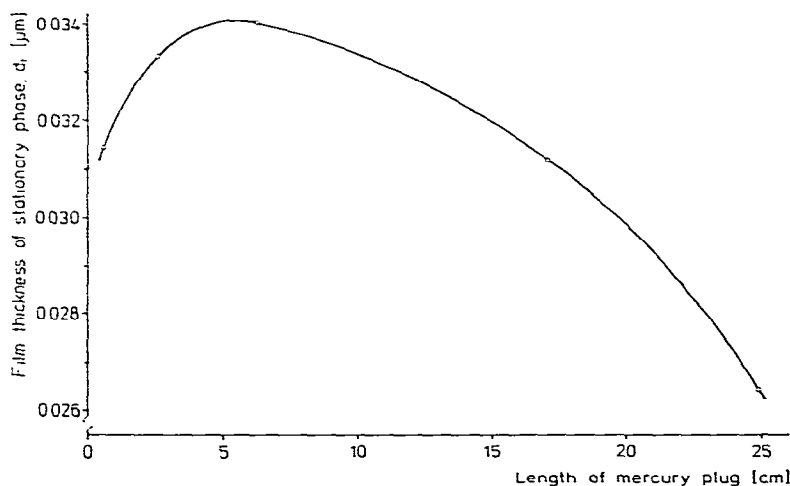

Fig. 3. The effect of the mercury-plug length on the film thickness of the stationary phase (based on ref. 12). The columns were etched with $HCl_{(g)}$ and coated with a 3% (w/v) solution of SE-30 in dichloromethane. The linear coating velocity of the plug was 0.74 cm/sec. Column I.D., 0.238 mm.

columns can only be expected when the same length of mercury is pushing the coating solution.

Gas chromatography of aromatic amines

The development of the splitless injection technique for capillary columns[14] has extended the possibilities for chromatographing trace amounts of organic compounds. The technique generally involves use of non-polar solvents, such as *n*-alkanes, carbon disulphide or chlorinated hydrocarbons. Aromatic amines however, are poorly soluble in, *e.g.*, *n*-alkanes. Chlorinated hydrocarbons, such as dichloro-
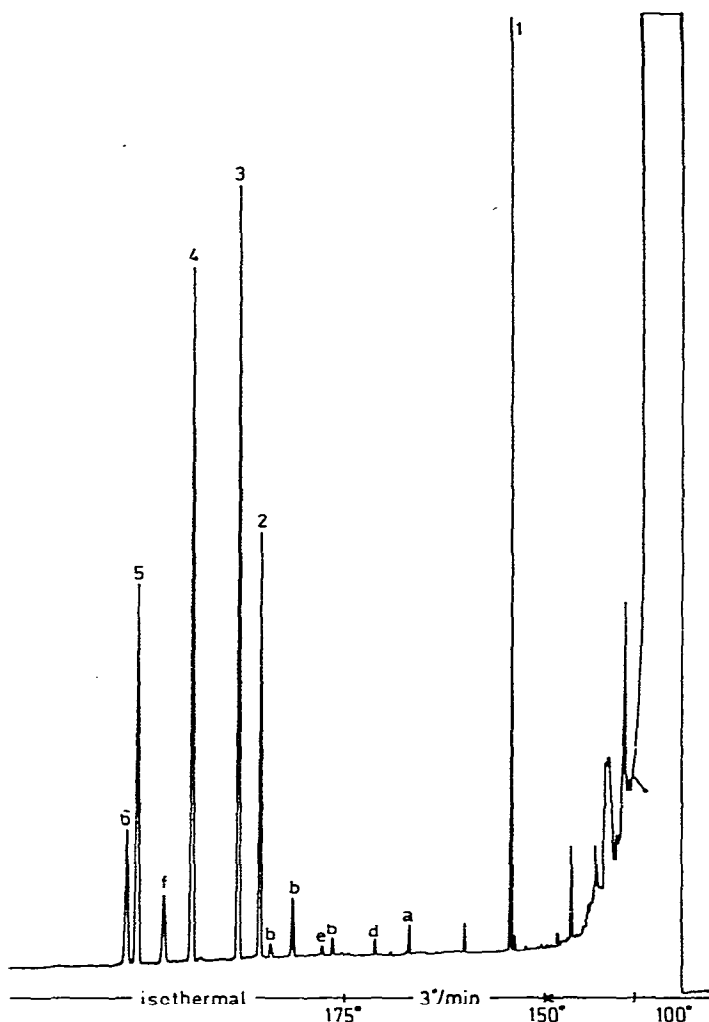
Fig. 4. Separation of AA on a basic wall-coated, open-tubular, glass capillary column (37 m × 0.32 mm I.D.); stationary phase Carbowax 20M. Splitless injection of 1 μl at 100°. Carrier gas, H_2 at 0.8 kp/cm². Injector and detector at 200°. Carlo Erba Fractovap 2350 /FID chromatograph; Onmi-Scribe recorder, 1 mV full-scale. Chart speed, 6 mm/min. Solvent: 2-butanone. Peak identification: 1 = 1,2-diaminobenzene; 2 = 2,4-diaminotoluene; 3 = diphenylamine; 4 = 1-aminonaphthalene; 5 = 2-aminonaphthalene; 6 = 2,4-diamino 1-methoxybenzene; a, b, d, e and f are impurities in 1, 2, 4, 5 and 6, respectively.

methane and chloroform are suitable solvents, but they are less desirable when a nitrogen-sensitive detector is used because ". . . chlorinated solvents cause a reversible sensitivity loss on the nitrogen–phosphorus detector . . ."[15].

On a suggestion from Grimmer[16], we now use 2-butanone for the splitless injection of AA; this ketone is somewhat polar and is a good solvent for AA. Of the different column temperatures tested to achieve optimum injection conditions, operation at 60, 80 and 100° all gave similar symmetrical peaks, whereas a column temperature of 120° showed incipient non-ideal peak symmetry for the lower-boiling AA, owing to a poor solvent effect[17]. A column temperature of 100° was adopted as a compromise, since low column temperatures and polar solvents is a combination to be used carefully if long column life is desired[18]. In Fig. 4 is shown the separation of a standard mixture of six AA (recrystallization later removed some of the impurities).

The preliminary results reported in this paper can at best be described as promising, and will be followed by studies on, *e.g.*, the stability of AA in solution and in the GC system, the detection limits ,the choice of internal standards, and the usefulness of the nitrogen detector. The nitrogen detector permits attainment of lower detection limits, and its selectivity for nitrogen-containing compounds might shorten the clean-up procedures in the analysis of AA. However, complete validation of the method can only be achieved through the analysis of actual samples.

ACKNOWLEDGEMENTS

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