407. *The Behaviour of Ammonia in Gas Chromatography. Part I. Ammine Formation in Columns containing Solutions of Silver Nitrate in Benzyl Cyanide.*

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When ammonia is passed into a freshly packed column containing silver nitrate in benzyl cyanide, it is permanently absorbed. After this absorption, the column retards further samples to produce a chromatogram consisting of a peak followed by a lower plateau. Decrease in sample size causes the peak to shrink until, at a critical sample size, it vanishes, leaving only the plateau. These results are interpreted as indicating the formation of a lower, stable ammine and a higher, unstable one related by the reaction $AgZ(NH_3)_x + 0{\cdot}5NH_3 \rightleftharpoons AgZ(NH_3)_{x+0{\cdot}5}$, the dissociation pressure of the higher ammine being approximately $5{\cdot}7 \times 10^{-3}$ atm.

Solutions of silver salts have been used as fixed phases in gas-liquid chromatography for the separation of olefins and other organic compounds.[1] Since such salts form ammines, their solutions suggest themselves for the chromatography of gaseous mixtures containing ammonia, and their use in this way has yielded unusual chromatograms which can be interpreted in terms of ammine formation. The results reported here were obtained at room temperature with solutions of silver nitrate in benzyl cyanide, and indicate the formation of at least two ammines, as is common with silver salts.[2]

Packings were generally prepared from 150·0 g. of fine glass beads as support, 5·00 ml. of benzyl cyanide, and a weighed amount (20—60 mg.) of silver nitrate, and packed by vibration in three weighed sections 90·0, 81·0, and 83·0 cm. long. Since the packings were not free-flowing, it was not possible to obtain uniform columns (linear density varied from 0·512 to 0·542 g. cm.$^{-1}$, permeability[3] by up to 22% from mean value). Coarser beads could be more

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[1] Bradford, Harvey, and Chalkley, *J. Inst. Petroleum*, 1955, **41**, 80; van de Craats, *Analyt. Chim. Acta*, 1956, **14**, 136; Gil-Av, Herling, and Shabtai, *Chem. and Ind.*, 1957, 1483; Tenney, *Analyt. Chem.*, 1958, **30**, 2; Bednas and Russell, *Canad. J. Chem.*, 1958, **36**, 1272; Phillips in " Gas Chromatography " (Coates, Noebels, and Fagerson, eds.), Academic Press Inc., New York, 1958, p. 51.

[2] " International Critical Tables," McGraw-Hill Book Company Inc., New York, 1930, Vol. VII, pp. 267—269.

[3] Keulemans, " Gas Chromatography," Reinhold Publishing Corporation, New York, 1957, Chapter 5.

uniformly packed, but gave poor results because of their small specific area. Crushed fire-brick adsorbed ammonia too strongly for use as a support; impregnation with alkali reduced adsorption, but was not used because of possible reaction of the alkali with the silver salt.

Nitrogen was used as carrier gas and its flow-rate corrected to ml. min.$^{-1}$ of dry gas at column temperature and atmospheric pressure.

RESULTS

A new packing absorbs a small amount of ammonia permanently, as is shown by non-emergence of a small sample. The amount absorbed cannot be measured, because the absorption is slow and extends over the passage of several samples, as is shown by a gradual approach of the chromatograms to reproducibility. A packing rich in silver nitrate gives reproducible results only after it has "matured" for a few days after passage of a few samples.

FIG. 1.

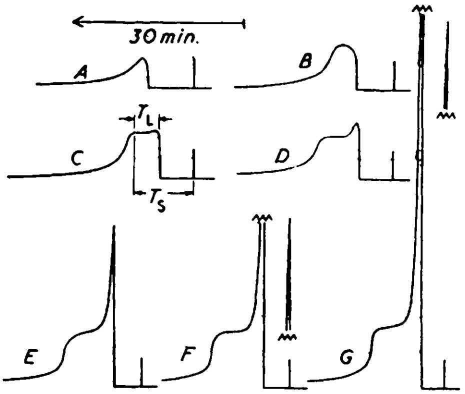

FIG. 2.

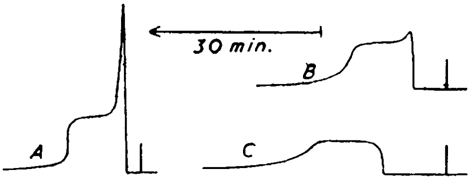

FIG. 1. *Ammonia chromatograms with mean linear concentration of silver nitrate,* 0·071 *mg. cm.*$^{-1}$; *column length,* 254·0 *cm.*; *carrier flow-rate,* 34·3—34·8 *cm.*^{3} *min.*$^{-1}$; *column temperature,* 17·4—19·8°; *sample size, cm.*^{3} (*N.T.P.*), *A,* 1·00; *B,* 1·50; *C,* 1·69; *D,* 2·00; *E,* 2·50; *F,* 3·00; *G,* 3·50. *Injection indicated by vertical stroke.*

FIG. 2. *Ammonia chromatograms with mean linear concentration of silver nitrate,* 0·196 *mg. cm.*$^{-1}$; *column length, cm., A,* 90·0; *B,* 171·0; *C,* 254·0; *carrier flow-rate,* 34·1—34·3 *cm.*^{3} *min.*$^{-1}$; *column temperature,* 17·7—20·3°; *sample size,* 2·50 *cm.*^{3} (*N.T.P.*). *Injection indicated by vertical stroke.*

FIG. 3.

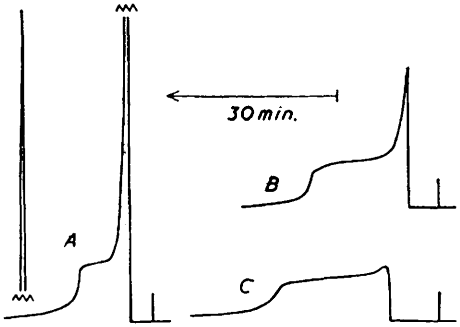

FIG. 3. *Ammonia chromatograms with mean linear concentration of silver nitrate, mg. cm.*$^{-1}$, *A,* 0·071; *B,* 0·134; *C,* 0·196; *column length,* 254·0 *cm.*; *carrier flow-rate,* 34·1—34·8 *cm.*^{3} *min.*$^{-1}$; *column temperature,* 18·8—19·8°, *sample size,* 4·00 *cm.*^{3} (*N.T.P.*). *Injection indicated by vertical stroke.*

112 chromatograms were obtained with matured packings and typical examples are shown in Figs. 1—3. Fig. 1 shows the effect of sample size. For a given packing and column length, there is a reproducible critical sample size giving a plateau followed by a "tail" (Fig. 1*C*), while samples larger than the critical produce a peak superimposed on the front of the plateau. The height of the peak grows rapidly with increase in sample size, while the plateau changes little. Reduction of sample size below the critical causes the plateau to decay from both ends. Figs. 2 and 3 show that increase in column length and increase in silver nitrate concentration both cause the plateau to grow at the expense of the peak. Decrease in carrier flow-rate merely stretches the chromatogram in the direction of the time axis.

DISCUSSION

Since the colour of a packing changes from white to pale mauve soon after preparation, it is uncertain whether the silver nitrate persists as such, and the salt in the column is therefore represented as AgZ. It is suggested that the absorption of ammonia by a new column is due to the formation of a stable ammine $AgZ(NH_3)_x$, while a matured column retards ammonia by the reaction

$$AgZ(NH_3)_x + yNH_3 \rightleftharpoons AgZ(NH_3)_{x+y}$$

for which the equilibrium ammonia pressure is p. A sample is injected at a pressure higher than p and moves rapidly through the column as a narrow zone (I), which continually loses ammonia to a slower-moving zone (II) in which ammonia is in equilibrium with $AgZ(NH_3)_x$ and $AgZ(NH_3)_{x+y}$ and therefore exerts pressure p. The emergence of zone I is recorded as a peak and that of zone II as a plateau. Let c = concentration of ammonia in fixed phase, c_1 = value of c corresponding to complete conversion of $AgZ(NH_3)_x$ into $AgZ(NH_3)_{x+y}$. Then $c = c_1$ immediately behind zone I and $c \ngtr c_1$ throughout zone II. If $c < c_1$ in any part of zone II, then that part moves faster than where $c = c_1$ and moves up to zone I. Thus $c = c_1$ throughout zone II. Following zone II there is a zone (III) in which the ammonia pressure is less than p and $c < c_1$, and whose emergence is recorded as a " tail."

Quantitative treatment of a chromatogram like Fig. 1*C* gives p and y. Such a chromatogram is obtained when zone I has just vanished upon reaching the end of the column. At this instant, zone II extends a distance L_1 * upwards from the end of the column. Apportionment by area measurements of the injected ammonia between the plateau and the tail gives the amount of ammonia emerging at partial pressure p, which can be found by applying the ideal-gas equation to the volume of gas escaping while the plateau is recorded. The amount of ammonia in both phases in zone II, excluding that in $AgZ(NH_3)_x$, is taken to be that producing the plateau. This is an approximation, since a small part of zone II degenerates into zone III while the plateau is recorded. The amount of ammonia in the fixed phase in zone II, excluding that in $AgZ(NH_3)_x$, is found by subtracting from the total the amount in the gas phase, found by applying the ideal-gas equation to the void volume in length L_1. Carman[4] reports the void volume to be 38% of total volume for randomly-packed, well-shaken spheres of equal size, but the packings were found to be more permeable to gas flow than the uncoated beads, and therefore their void volume is taken to be 50%. Since only a small fraction of the ammonia is in the gas phase, an error in the assumed void volume has little effect on the calculated amount of ammonia in the fixed phase. The amount of salt in zone II is found from L_1 and the density and composition of the packing.

L_1 is found from the emergence time $t_{\rm L}$ and final retention time $t_{\rm s}$ of the plateau (see Fig. 1*C*). If the pressure drop is low, so that the linear gas speed is nearly uniform through the column, and if the decay of the rear end of zone II is neglected, then the speed of the rear end is $L/t_{\rm s}$, where L = length of packing, and L_1 is traversed in time $t_{\rm L}$ and has the value $Lt_{\rm L}/t_{\rm s}$. Where the pressure drop is appreciable, the effect of compressibility on gas speed has to be taken into account, by means of equations developed by Keulemans.[3] Combination of his equations (5) and (10) gives

$$t_g = Kp_{\rm o}[(p_{\rm i}/p_{\rm o})^3 - 1]/3\eta u_{\rm o}^2,$$

where t_g = residence time of carrier gas, K = permeability of packing (assumed uniform), η = dynamic viscosity of carrier gas, $u_{\rm o}$ = linear speed of gas at column outlet, $p_{\rm i}$ = inlet

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* Symbols used by Keulemans[3] are adopted here with slight modifications.

[4] Carman, " Chemical Constitution and Properties of Engineering Materials," Edward Arnold and Co., London, 1949, p. 28.

pressure, p_o = outlet pressure. Since the speed of zone II is a constant fraction r of the carrier speed,

$$t_s = Kp_o[(p_i/p_o)^3 - 1]/3\eta u_o^2 r \quad . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

and

$$t_L = Kp_o[(p_L/p_o)^3 - 1]/3\eta u_o^2 r \quad . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

where p_L = pressure at distance L_1 from outlet, decay of zone II being neglected. From (1) and (2),

$$(p_L/p_o)^3 = 1 + t_L[(p_i/p_o)^3 - 1]/t_s \quad . \; . \; . \; . \; . \; . \; . \quad (3)$$

Keulemans's equation (6) can be modified to

$$L_1/L = [(p_L/p_o)^2 - 1]/[(p_i p_o)^2 - 1] \quad . \; . \; . \; . \; . \; . \; . \quad (4)$$

Equations (3) and (4) are used to find L_1 from measured values of t_L, t_s, p_i, p_o, and L.

Dissociation pressure and composition of ammine.

$AgNO_3$ *	Packing length (cm.)	Flow-rate (cm.^{3} min.$^{-1}$)	Pressure drop (mm.)	Column temp.	10^3p (atm.)	y
0·071	254·0	34·8	304	19·6°	6·3	0·77
,,	254·0	34·3	303	19·2	6·2	0·74
0·134	254·0	33·8	203	20·0	5·7	0·53
0·168	257·9	34·9	309	17·0	5·5	0·53
0·196	254·0	34·0	228	18·6	5·1	0·45
,,	254·0	34·2	229	20·2	5·3	0·43
,,	254·0	34·3	230	19·3	5·3	0·45
,,	171·0	34·2	158	20·1	5·8	0·48
,,	171·0	16·2	78·1	20·5	6·2	0·51
,,	90·0	7·84	19·9	20·6	5·8	0·60

* Mean linear concentration of silver nitrate (mg. cm.$^{-1}$).

The Table shows values of p and y calculated from chromatograms including some which differ slightly from the type of Fig. 1*C*, allowance being made in ammonia apportionment for areas not belonging to the plateau. Mean values and standard deviations are: 10^3p, 5·7, 0·42 atm.; y, 0·50, 0·056. While the large standard deviations reflect the approximate nature of the calculations, p and y do not vary systematically with the controlled variables, except that the lean packing (0·071 mg. cm.$^{-1}$ of silver nitrate) gives high values for y, possibly because adsorption and solution play a larger rôle relative to ammine formation. These values are excluded from the calculation of the mean and standard deviation. The mean value of y shows the equation for ammine formation to be

$$AgZ(NH_3)_x + 0{\cdot}5NH_3 \rightleftharpoons AgZ(NH_3)_{x+0{\cdot}5}.$$

Other workers [1] have not observed the plateau. They have used concentrated solutions of silver salts and their peaks are probably lower than the corresponding plateaux, like the peak of Fig. 1*A*.

EXPERIMENTAL

Apparatus.—The gas-chromatographic apparatus was of conventional type, with glass columns of 6 mm. i.d., flow regulator, manometer, sample injector similar to Harrison's,[5] katharometer and bridge circuit (supplied by Messrs. Griffin and George Ltd., Wembley), recorder (Honeywell Brown, 3 mv f.s.d.), and soap-film flow-meter discharging to atmosphere. The recorder chart speed was 6 in. hr.$^{-1}$ and sensitivity [6] 52 ml. mv mg.$^{-1}$.

Solid Support.—Glass beads ("Ballotini," Grade 15, 0·10 mm. diam. and Grade 8a, 0·40 mm. diam., supplied by the English Glass Co. Ltd., Leicester) as purchased retained ammonia too strongly for use as a support; treatment with acid or alkali (but not with water) reduced the retentivity. The material used was boiled briefly with 30% sodium hydroxide solution, washed thoroughly with distilled water, and dried in an oven. When uncoated and when

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[5] Harrison in "Vapour Phase Chromatography" (Desty, ed.), Butterworths Scientific Publications, London, 1957, p. 332.

[6] Johnson and Stross, *Analyt. Chem.*, 1958, **30**, 1586.

coated with the same proportion of benzyl cyanide as used in the test packings, it gave tailing ammonia peaks with low retention time.

Packings.—The packings were made by dissolving silver nitrate (M. and B. Laboratory Chemical, assay $\nless 99{\cdot}8\%$) in benzyl cyanide (B.D.H. Laboratory Reagent), diluting with ethyl ether (Riedel-de Haën, Analytical Quality), making into a slurry with " Ballotini," Grade 15, and evaporating off the ether at room temperature with a stream of dry nitrogen. Dilution with ether caused the solutions to turn milky. The coarser beads could be coated without ether, and gave the same chromatograms as when ether was used.

Ammonia.—This was obtained by mixing concentrated solutions of ammonium nitrate and of sodium hydroxide, swept with nitrogen through calcium oxide desiccant, and condensed in a trap containing calcium oxide. The trap was evacuated while cold and left overnight at room temperature, after which the dry ammonia was condensed into an evacuated reservoir. Gas chromatography showed the ammonia to contain traces of impurities.

Carrier Gas.—Cylinder nitrogen, dried with phosphoric oxide, was used.

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