STUDIES IN THE GAS CHROMATOGRAPHY OF AMMONIA

with special reference to packings containing solutions of

silver salts in some organic solvents

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by

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PREFACE

I should like to express my gratitude to Dr. A.H. Spcng for offering me the opportunity to do the work described in this thesis and giving me help and advice throughout its course.

My thanks are also due to the entire staff of the Department of Chemistry for constant assistance, to Mr. G. Delpierre for allowing me to use his glassware for distilling solvents, to Mr. D. Lucas for making me a small copper bucket, and to my wife for helping to check stencils.

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SUMMARY

It has been found that the gas chromatography of ammonia on certain fixed phases containing salts yields chromatograms consisting of a peak followed by a plateau or a succession of plateaux of progressively decreasing height. Such chromatograms have been interpreted in terms of ammine formation in the column, and methods have been theoretically elaborated for using measurements on the chromatograms to find the dissociation pressures of the ammines and the ratios of ammonia taken up to silver in the fixed phase. These methods require the calibration of the detector, so that ammonia partial pressures can be found from chromatogram heights, and this has been done by a chromatographic method. In most cases, the ratio of ammonia to silver in the fixed phase does not yield conclusive information on ammine composition, because there is usually evidence that the salt is present in different forms or is only partially converted to ammine.

Most attention has been devoted to packings containing silver salts dissolved in organic liquids. Solutions of silver nitrate in benzyl cyanide and benzonitrile, and of silver perchlorate in benzyl cyanide, benzonitrile, fenchone and tetralin have been found to yield chromatograms with plateaux, and a study of these has shown that both the anion and the solvent influence ammine formation. All these solutions react with ammonia to form a white precipitate and therefore act as heterogeneous fixed phases. New packings absorb some ammonia, but this is slowly removed by a current of carrier gas; the absorption is ascribed to the formation of lower ammines having dissociation pressures too low to be registered by the detector. The apparent compositions of the lower ammines have been determined by measuring the initial absorption, and their dissociation pressures

have been found for some packings by measuring the rate of removal of ammonia by a current of carrier gas. Complicated ageing processes take place in columns containing silver nitrate and silver perchlorate in benzyl cyanide.

A survey of all the dissociation pressures determined shows that these fall into three groups, at roughly 10^{-4}, 10^{-2} and 10^{-1} atm. The highest and lowest groups are shown by all the systems studied, but the middle group only by solutions in benzyl cyanide. A more detailed comparison of pressures in the highest group shows that silver nitrate in a given solvent forms an ammine with a dissociation pressure higher than that of the ammine formed by silver perchlorate in the same solvent. Although the stoichiometric data obtained are very rough, there is some indication that ammines of similar composition are formed in different solutions.

In contrast to the solutions enumerated above, silver nitrate and silver perchlorate in m-toluidine form no precipitate with ~~ammonia~~, do not absorb ammonia initially and do not give plateau chromatograms. On these solutions, ammonia has a final retention volume that is independent of sample size.

Experiments with silver perchlorate in mixtures of fenchone and benzyl cyanide, silver nitrate in mixtures of benzonitrile and m-toluidine, and silver nitrate and silver perchlorate together in benzonitrile have shown that these three-component systems produce chromatograms having some plateaux in common with the chromatograms of the corresponding two-component systems, but also showing plateaux not occurring in the latter.

A few tensimetric experiments have been performed with ammonia and solutions of silver nitrate in benzonitrile, and have produced results in rough agreement with the gas-chromatographic results.

Plateau chromatograms have also been obtained with granular lead bromide and lead chloride; it appears that ammine formation is confined to the surface of these salts.

Some packings containing salts have been found to give ammonia chromatograms showing two peaks, of which the first increases in size with increasing humidity of the carrier gas, and is ascribed to moisture taken up by the packing from the carrier and later displaced by the ammonia sample.

CONTENTS

INTRODUCTION

The technique known as gas chromatography has proved to be a very effective method of separating closely similar substances, and work was started in this Department in an attempt to use it for the separation of $N^{14}H_3$ and $N^{15}H_3$. This work showed that ammonia, because of its high polarity and ability to form complexes, has unusual gas-chromatographic characteristics. The elucidation of these characteristics was considered a necessary preliminary for the separation of $N^{14}H_3$ and $N^{15}H_3$ and has provided the main theme of this thesis.

Most of the results described here were obtained with solutions of silver salts in high-boiling organic solvents as the fixed phase. When an ammonia sample is chromatographed on such a fixed phase, it usually emerges in a way that can be explained by the formation of a solid ammine precipitated from the solution. It will be shown that quantitative treatment of the chromatogram can give the dissociation pressure of the ammine and some information about its composition.

Section 1 of this thesis is general and introductory, and provides the background for the present work by describing other applications of gas chromatography and other methods of studying ammines. Section 2 gives the theory needed for the interpretation of the experimental results reported in Section 4, while Section 3 describes the apparatus and procedures used. Correlations of the results and a comparison of gas chromatography with the other methods of studying ammines are presented in Section 5.

SECTION 1

GENERAL

1.1 The history, variants and applications of gas chromatography

Chromatography has been defined[1] as "a physical method of separation, in which the components to be separated are distributed between two phases, one of these phases constituting a stationary bed of large surface area, the other being a fluid that percolates through the stationary bed". If the "fluid that percolates" and the "components to be separated" are gases, the process is gas chromatography, of which the earliest known description[2] was written in 1512 by a Strasbourg surgeon named Brunschwig, who passed the vapour from spirit through a layer of sponge soaked in olive oil. A small amount of pure ethyl alcohol emerged from the sponge before steam came through as well. This technique fell into disuse after the 17th century and gas chromatography was not revived till the 20th century.

In 1941 Martin and Synge[3] suggested the separation of a gaseous mixture by sweeping it with an inert carrier gas through a column containing a liquid solvent supported on a porous, granular solid. The solvent would retard some components of the mixture more than others and thus bring about a separation. This technique later acquired the name of gas-liquid chromatography and was first realized experimentally by James and Martin[4] in 1952. Meanwhile, Hesse and his co-workers[5] had in 1941 used a similar method with a solid adsorbent instead of the supported liquid. This method is now called gas-solid chromatography and, together with the method of Martin and Synge, is described as elution chromatography.

In another variant of gas-solid chromatography, described as displacement chromatography, a strongly adsorbed vapour at constant pressure is made to move through the column behind the mixture to be analysed. The strongly adsorbed substance displaces the mixture from the solid and each component of the mixture acts as a displacer for the components that are less strongly adsorbed than itself. A series of adjacent zones of components thus emerges from the column, the length of each zone being proportional to the amount of the corresponding component. After early work (1943) by Turner[6], Claesson[7] published a careful study of displacement chromatography in 1946.

Claesson[7] also describes the technique of frontal chromatography, in which a continuous stream of the mixture to be analysed is fed to the column and emerges as a series of zones. The first of these zones contains only one component, the second, two components, and so on, till the last zone, which contains the original mixture. Brunschwig's purification of alcohol was frontal chromatography.

Chromathermography[8] is an elaboration of gas chromatography in which an annular oven with an axial temperature gradient moves along the column, the axes of oven and column being coincident. The sample to be analysed is driven along the column by the heat of the oven, and each component occupies the position in the oven where the temperature is just high enough to expel it from the column packing.

The pioneering work mentioned in this sub-section has been followed by such tremendous development of gas chromatography that comprehensive bibliographies on the subject now contain hundreds of references.

The definition of chromatography quoted above stresses the purpose for which gas chromatography has been mainly used, viz separation of mixtures. Such separation may be for analytical purposes, either qualitative or quantitative, or, on a larger scale, for preparative purposes. Another important application of gas chromatography is the determination of distribution functions and quantities derived from them, such as activity coefficients and heats of solution or adsorption.

1.2 The determination of distribution functions by gas chromatography

Adsorption isotherms are one class of distribution function and have been determined from frontal chromatograms of single substances [7, 9, 10, 11]. Such a chromatogram is obtained when carrier gas containing vapour G at known partial pressure P is passed into a column of adsorbent, in which G remains at partial pressure P and each gram of adsorbent binds w grams of G. At time t after the flow is started, the vapour front emerges from the downstream end of the column. Then

$$w = \frac{1}{W}\left(\frac{PtV_tM}{RT} - D\right),$$

where W = weight of adsorbent in column

V_t = volumetric flow-rate of gas entering column

M = molecular weight of G

R = gas constant

T = absolute temperature at which V_t is measured

D = weight of G in gas phase in column.

Griffiths and Phillips[12] describe the determination of vapour pressures of liquids from displacement chromatograms. Carrier gas is saturated with the vapour (G) whose pressure (P) is desired and passed through a column of adsorbent that retains the vapour. A displacer is then passed through the column and the weight (w) of G found from the length of the displaced zone of G. P is calculated from

$$P = \frac{w R T}{M t V_t}, \quad \text{------------} \quad (i)$$

where R = gas constant

T = absolute temperature of saturator

M = molecular weight of G

t = time for which saturation of carrier took place

V_t = volumetric flow-rate of gas leaving saturator.

The movement of a vapour G through a gas-liquid chromatographic column is governed by the partition coefficient (k), a distribution function defined by

$$k = \frac{\text{weight of G per unit volume of column liquid}}{\text{weight of G per unit volume of carrier gas}}.$$

k is related to easily measurable quantities by the equation (see 2.2, p. 9)

$$V_r^{\circ} = k V_f + V_g, \quad \text{------------} \quad (ii)$$

where V_r^o = volume of carrier gas (corrected for pressure drop) needed to sweep G through column

V_f = volume of liquid phase in column

V_g = volume of gas phase in column.

Values of k (or derived quantities) found from equation (ii) have been reported by several workers[10, 13, 14, 15, 16].

The methods of calculation evolved for obtaining information about ammines (2.4, 2.5, 2.6) have some features in common with the methods described in this sub-section.

1.3 Non-chromatographic methods of studying ammines and other complexes of gases and solids

The method which has been most widely used for determining the dissociation pressures of complexes is direct manometric measurement in a tensimeter[17, 18, 19, 20, 21].

Usually the composition of the complex is determined separately by analysis, but some workers have followed changes of composition by measuring the amount of gas given off or absorbed by the complex while in the tensimeter[18, 19]. A few rough tensimetric experiments have been performed in the present work to verify gas-chromatographic measurements on ammines.

In the indirect method[20, 22, 23], the complex and its dissociation products are allowed to come to equilibrium with a supernatant liquid B, in which only the gaseous product G is soluble and over which the pressure of G is known as a function of concentration. The pressure of G over the solution is the dissociation pressure of the complex, and is found by determining the concentration of G in the solution. In a variant of the method, the complex and liquid B are not in contact, but exchange G through an intervening gaseous phase; an example is the determination of the dissociation pressure of a hydrate by finding the concentration of sulphuric acid in the presence of which it does not gain or lose weight[19, 23, 24].

The gas-current saturation method[21,25] resembles the procedure of Griffiths and Phillips described in 1.2, p.4. An inert gas is passed for time t at volumetric flow-rate V_t through a quantity of dissociating complex sufficient to saturate it with the gaseous dissociation product G. The saturated gas is stripped of G by a suitable reagent, whose increase in weight (w) is found, and the dissociation pressure (P) is calculated from equation (i), p.5 .

SECTION 2

THEORETICAL CONSIDERATIONS

2.1 Symbols used

The symbols adopted in this section are based on those used by Keulemans[26], with some modifications necessitated by differences in subject matter. All symbols are defined where they are introduced. The following is an alphabetical list for easy reference :-

A	Area of chromatogram
a	Cross-sectional area of gas phase
C	Calibration factor of detector
c	Recorder chart speed
F	Substance forming fixed phase
f	Moles of F in column
G	Substance carried through column by moving phase
G_f	Moles of G per unit length of fixed phase
G_f'	Value of G_f corresponding to complete conversion of F to $F.G_y$
G_g	Moles of G per unit length of moving phase
G_g'	Value of G_g corresponding to $P = P_d$
h	Height of experimental chromatogram at any instant
K	Permeability of packing
k	Partition coefficient
L	Length of column
L_1	Length of zone II when it starts emerging
$m, m + 1$	Serial numbers of chromatograms
n	Sample size in moles
P	Pressure of G in column

p_d	Dissociation pressure of $F.G_y$
p	Pressure of carrier gas
p_{at}	Atmospheric pressure
p_i	Value of p at column inlet
p_L	Value of p at distance L_1 from outlet
p_o	Value of p at column outlet
R	Gas constant
T	Absolute temperature
t	Time after injection of G
t_b	Value of t when zone II starts emerging
t_e	Value of t when emergence of zone II is complete
t_g	Residence time of carrier gas
t_h	Value of t at half plateau height
t_m	Time between chromatograms m and m + 1
V_c	$(V_r^o - V_g)/f$
V_f	Volume of liquid fixed phase in column
V_g	Volume of moving phase in column
V_r	Retention volume of G
V_r^o	Retention volume of G corrected for pressure drop
V_t	Volumetric flow-rate of carrier gas
v	Sample volume
x	Distance from upstream end of column
y	Molar ratio of G to F in $F.G_y$
δL	Element of column length
η	Dynamic viscosity of carrier gas

2.2 <u>General</u>

In all chromatography the substance or mixture being studied is distributed between the fixed and moving phases. This distribution governs the movement of substances through a column, and the first step in this theoretical discussion will be to relate the speed with which a substance traverses a column to its distribution between the phases.

Consider a uniformly packed column of uniform bore, in which the moving phase occupies a volume of V_g cm^3 and is an incompressible fluid flowing at a volumetric flow-rate of V_t cm^3 min^{-1}. It is evident that a small element of the fluid flows through the column in V_g/V_t min. Let a small quantity of substance G, having some affinity for the fixed phase, be introduced at the upstream end of the column so as to occupy uniformly a volume element of the packing bounded by the walls of the tube and two cross-sectional planes distant δL from each other. Assume that substance G is immediately distributed at equilibrium between the two phases, with $G_f\delta L$ mole in the fixed phase and $G_g\delta L$ mole in the moving phase, G_f and G_g being linear concentrations. A molecule of G spends in each phase a time proportional to the amount of G in that phase, and thus spends in the moving phase a fraction $G_g/(G_f + G_g)$ of each minute, during which it is carried along by the moving phase at the speed of the latter. If it be assumed that G does not migrate while in the fixed phase, it follows that the zone of G has an average speed of movement through the column that is a fraction $G_g/(G_f + G_g)$ of the speed of the moving phase. Therefore G takes $(G_f + G_g)/G_g$ times as long as the moving phase to traverse the column, i.e. it takes $\frac{V_g}{V_t} \cdot \frac{G_f + G_g}{G_g}$ min. During this time a volume V_r cm^3 of the moving phase, called the retention volume of substance G, leaves the column. It is evident that $V_r = V_t \cdot \frac{V_g}{V_t} \cdot \frac{G_f + G_g}{G_g}$, or

$$V_r = V_g\left(\frac{G_f}{G_g} + 1\right). \qquad \text{(i)}$$

In gas chromatography the moving phase is not incompressible and its volumetric flow-rate increases from the upstream to the downstream end of the column. If the ideal-gas equation be assumed to hold for the moving phase, it can be shown[27] that equation (i) holds when V_r is replaced by $V_r^{\circ} = \frac{3}{2}\,\frac{(p_i/p_o)^2 - 1}{(p_i/p_o)^3 - 1} \cdot V_r$,

where p_i = pressure of moving phase at column inlet

p_o = pressure of moving phase at column outlet.

$$\text{Thus } V_r^{\circ} = V_g\left(\frac{G_f}{G_g} + 1\right). \qquad \text{(ii)}$$

For gas-liquid chromatography, equation (ii) can be expressed in terms of the partition coefficient k, defined as

$$\frac{\text{weight of G per unit volume of fixed phase}}{\text{weight of G per unit volume of moving phase}}.$$

If the volume of the liquid fixed phase in the column is V_f, then, in a uniformly packed column, V_f/V_g is the volume ratio of the fixed and moving phases in the small length δL occupied by the zone of G. It follows from the definition of k that

$$G_f/G_g = kV_f/V_g\,. \qquad \text{(iii)}$$

Elimination of G_f/G_g from (ii) and (iii) gives

$$V_r^{\circ} = kV_f + V_g\,. \qquad \text{(iv)}$$

2.2. 1 Zone broadening

In practice the zone of G becomes broader as it moves along the column and its boundaries become diffuse.

The reasons for this are that (i) the tortuous channels through the packing provide many paths of different lengths for the flowing gas; (ii) molecular diffusion of G along the column is superimposed on the bulk transport by the carrier gas; (iii) rates of transfer of G between the phases are finite[28]. The resulting differential chromatogram (plot of concentration of G in column effluent against time) is a peak, which is symmetrical if G_f/G_g is independent of G_g. It has been found[10] that V_r^o for the peak maximum obeys equation (iv).

2. 2. 2 Effect of varying distribution between fixed and moving phases

If G_f/G_g depends on G_g, the chromatogram is asymmetrical and V_r^o for the peak maximum depends on the amount of G injected. In gas-solid chromatography, G_f/G_g almost always decreases as G_g increases (adsorption isotherm concave to pressure axis) and V_r^o decreases with G_f/G_g, according to equation (ii). Thus parts of the zone of G where G_g is high move faster than parts where G_g is lower, and the chromatogram has a high, steep front and long "tail". Also, large samples of G emerge sooner than small ones, since G_g increases with sample size if injection is rapid.

2. 3 Theoretical prediction of the chromatogram obtained with a complex-forming fixed phase

In gas chromatography, if the fixed phase is a solid substance F that reversibly forms a solid complex with the injected vapour G:

$$F(s) + y\,G(g) \rightleftharpoons F.G_y(s), \text{ - - - - - - - - - - - - - - } (v)$$

then, at a given temperature, G has a fixed pressure when in equilibrium with both F and $F.G_y$. This is the dissociation pressure (P_d) of $F.G_y$. The chromatographic behaviour of G can be predicted by considering how reaction (v) controls G_f and G_g.

2.3.1 Ideal chromatogram

Assume that the zone-broadening factors mentioned in 2.2.1 are absent and G is introduced in the ideal way described in 2.2. Let the pressure (P) of G be higher than P_d, so that all F in the length δL is converted to $F.G_y$. This corresponds to a fixed value of G_f, say G_f'. As the region of high P moves along, it leaves the fixed phase in the form $F.G_y$. Dissociation of $F.G_y$ results in the presence of both F and $F.G_y$, which fixes P at P_d and G_g at a corresponding value G_g'. Thus the original zone of length δL separates into two zones: a fast-moving zone I, shorter than δL, in which $P > P_d$ and $G_f = G_f'$; and a slower zone II, in which $P = P_d$ and $G_f \leq G_f'$. It is easy to see that G_f cannot be much less than G_f' in zone II; for if it were so in any part of zone II, that part would have a G_f/G_g ratio less than G_f'/G_g' and would move ahead to zone I. Thus $G_f = G_f'$, nearly, throughout zone II. As zone I moves along, it gradually loses its G to zone II, so that I shrinks and II lengthens. When I has vanished, II continues to move unchanged at constant speed.

Fig. 1 shows P as a function of distance along the column and time (t) after injection of G. The cross-hatched areas are graphs of P against distance at different times. For a fixed point in the column, say M, the corresponding area MNOPQR is also the graph of P against t, if the axis of abscissae is reversed in direction and given a suitable scale. For the column outlet, the graph of P against t is the chromatogram, and shows high and low regions (or the latter only).

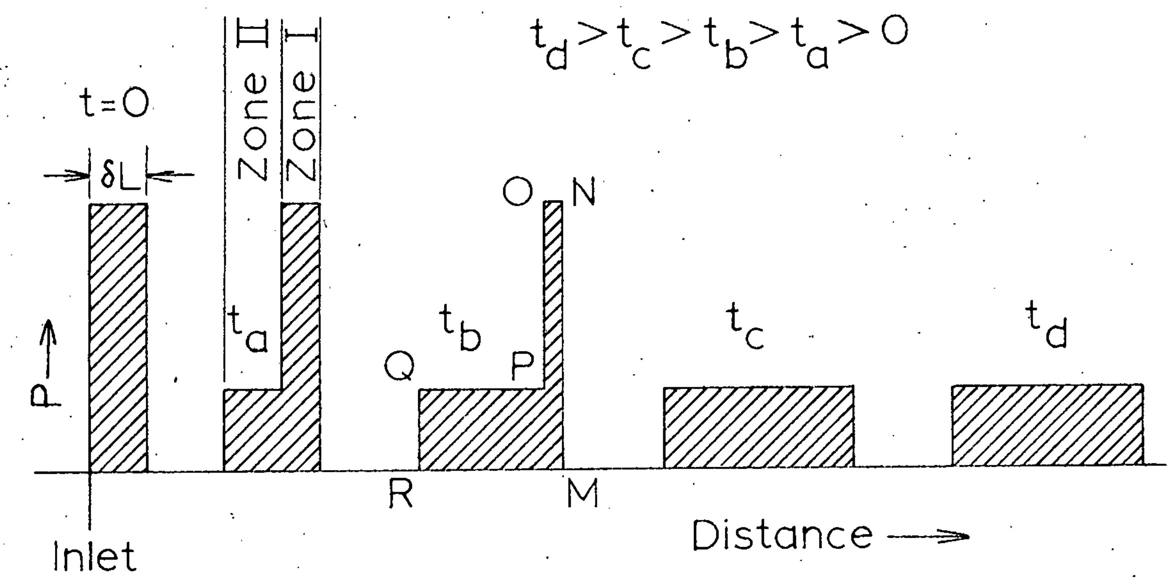

Figure 1. Complex-forming fixed phase – pressure of sample vapour as a function of time and distance along column.

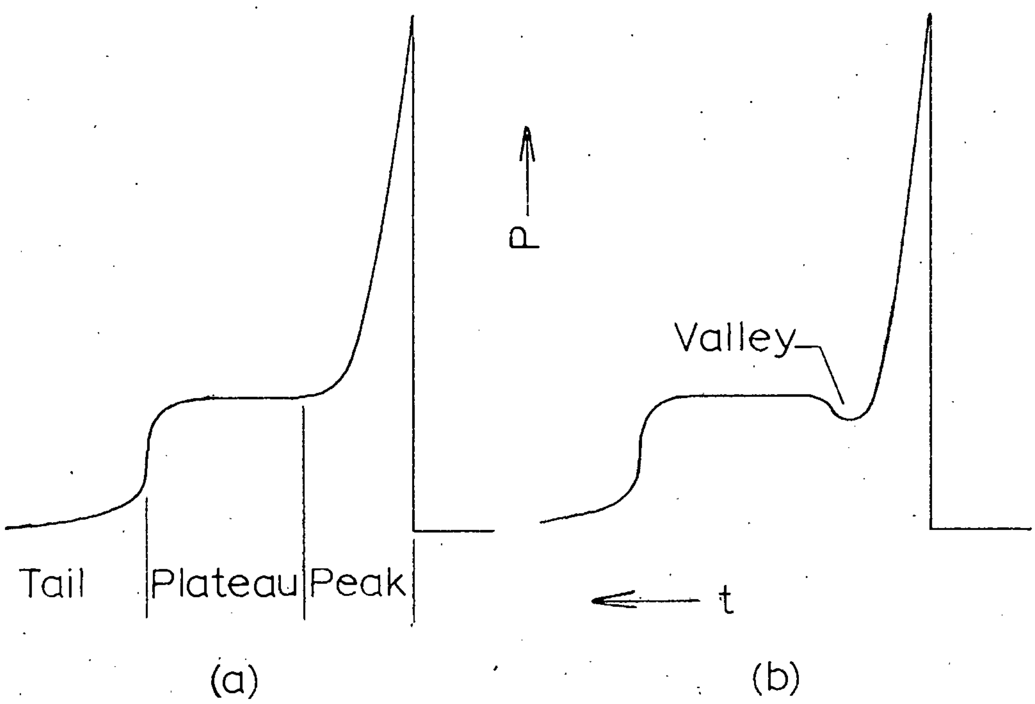

Figure 2. Complex-forming fixed phase – real chromatograms.

which will be designated I and II according to the corresponding zones in the column.

It is obvious that, for a given packing and fixed sample size, the sequence of cross-hatched areas in Fig. 1 illustrates the change produced in the chromatogram by increasing the column length. An increase in sample size, with a given packing and fixed column length, increases the area of region I, but leaves region II unchanged except for the slight encroachment by region I. An increase in the amount of F in the packing, other conditions remaining the same, causes region I to shrink and II to lengthen. Decrease of carrier flow-rate merely stretches the chromatogram in the direction of the time axis.

2.3.2 Real chromatogram

The factors mentioned in 2.2.1, p.11 , may be expected to cause some broadening and rounding of the graphs shown in Fig. 1. If, furthermore, F is supported on a solid which adsorbs G to some extent, the front of the chromatogram will remain steep and tailing will be accentuated (see 2.2.2, p.12). Thus a chromatogram like Fig. 2(a) may be expected. Such chromatograms have been obtained experimentally and their regions are conveniently named the "peak", "plateau" and "tail", as indicated in Fig. 2(a).

The further deviation from ideality shown in Fig. 2(b), a "valley", has been observed and ascribed to delayed decomposition of $F.G_y$. If this substance persists in a metastable state when $P<P_d$ and starts dissociating only when P is considerably less than P_d, there will be an intermediate zone, in which $P<P_d$ and $G_f=G_f'$, between zones I and II.

2.4 Calibration of the detector

Although Figs 1 and 2 show P as the ordinate, an experimental chromatogram has as ordinate not P, but some function of P. The type of detector used in the present work, the katharometer, is reported[29] to have a response which is usually proportional to P. This proportionality can be tested as follows.

Assume that the chromatogram height, h, at any instant is proportional to P at that instant, i.e.

$$P = Ch, \text{ - - - - - - - - - - - - - - - - - - (vi)}$$

where C is a constant, the calibration factor of the detector. During a small interval of time, dt, the recorder chart moves a distance cdt, c being the chart speed, and a volume $V_t dt$ of gas leaves the column, V_t being measured at the column outlet. The amount, dn, of G in this gas is, by the ideal-gas equation, $PV_t dt/RT$ mole, where R is the gas constant and T the absolute temperature. By equation (vi),

$$\frac{PV_t dt}{RT} = \frac{ChV_t dt}{RT}$$

$$\text{so } dn = \frac{ChV_t dt}{RT} = \frac{CV_t(hcdt)}{cRT}$$

Now hc dt is the element of area, dA, added to the chromatogram during dt, so that

$$dn = \frac{CV_t dA}{cRT}.$$

Integration of this equation gives $n = \frac{CV_t A}{cRT}$, where n is the sample size and A the area of the chromatogram. Rearrangement gives

$$C = \frac{ncRT}{V_t A}. \text{ - - - - - - - - - - - - - - - - - - - (vii)}$$

If the value of C calculated from this equation is independent of the average height of the chromatogram, the assumption (vi) is valid.

The validity of (vi) has been established within certain ranges of the experimental variables (see 4.14.4, p.115) and the numerical value of C used to calculate P_d.

Equation (vii) can be modified to a more convenient form when sample injection is by syringe and the column is at room temperature. Under these conditions, $n = \frac{p_{at}v}{RT}$, where p_{at} is atmospheric pressure and v the sample volume. Substitution in (vii) gives $C = \frac{p_{at}v}{RT} \cdot \frac{cRT}{V_t A} = \frac{p_{at}vc}{V_t A}$. This becomes

$$C = \frac{3.34\ p_{at}V}{V_t A} \times 10^{-2}\ \text{atm cm}^{-1}, \quad \text{--------------------(viii)}$$

if c is 6 in. hr^{-1} (the speed most used in this work) and the units of the variables are p_{at}, mm Hg; v, cm^3; A, cm^2; V_t, $cm^3\ min^{-1}$.

2.5 The determination of complex composition

There are two methods of determining y in $F.G_y$, and they will be called Method 1 and Method 2. In 2.5.1 and 2.5.2 these methods are elaborated for ideal chromatograms, and in 2.5.3 their application to real chromatograms is discussed.

2.5.1 Method 1

Consider the ideal chromatogram shown in Fig. 3. At instant t_b, zone I has just left the column and zone II extends a distance L_1 upstream from the outlet. The total amount of G in zone II, $L_1(G_f^! + G_g^!)$, is $\frac{n(\text{area PQRS})}{\text{area MNOPQR}}$. The amount of G in the gas phase in zone II, $L_1 G_g^!$, can be calculated from P_d and the volume $(L_1 V_g/L)$ of that phase, L being the length of the column. $L_1 G_f^!$, the amount of G in $F.G_y$ in Zone II, can then be found by subtraction and divided by the amount of F in zone II (viz $L_1 f/L$, where f is the number of moles of F in the whole column) to find y.

L_1 can be found from t_b and t_e (see Fig. 3). If the pressure drop is low, so that the linear gas speed is nearly uniform through the column, then the speed of zone II is L/t_e, and L_1 is traversed in time $t_e - t_b$ and has the value $L(t_e - t_b)/t_e$. Where the pressure drop is appreciable, the effect of compressibility on gas speed can be taken into account by means of equations developed by Keulemans[27]. In the symbols

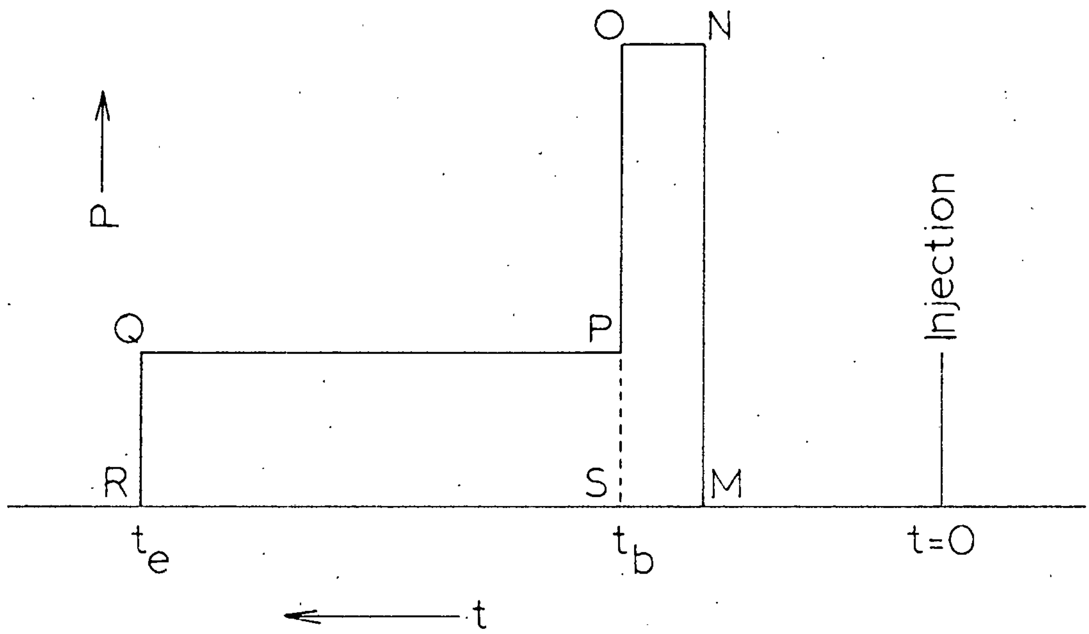

Figure 3. Ideal chromatogram showing quantities used in determining complex composition.

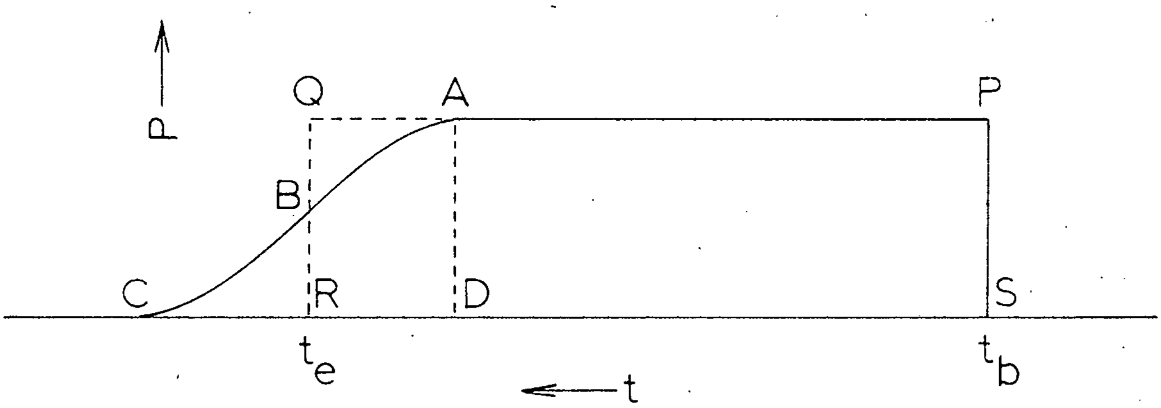

Figure 4. Reconstruction of ideal chromatogram.

used here, his equations (5) and (10) are

$$V_t\, p_o\, L = \frac{1}{2}\, a\, \frac{K}{\eta}\, (p_i^2 - p_o^2) \quad \ldots\ldots\ldots\ldots \quad \text{(ix)}$$

and
$$t_g = \frac{2}{3}\,\frac{V_g}{V_t} \cdot \frac{(p_i/p_o)^3 - 1}{(p_i/p_o)^2 - 1}, \quad \ldots\ldots\ldots \quad \text{(x)}$$

where a = cross-sectional area of gas phase, K = permeability of packing, η = dynamic viscosity of carrier gas, t_g = residence time of carrier gas. Division by p_o^2 converts (ix) to

$$\frac{V_t L}{p_o} = \frac{1}{2}\, a\, \frac{K}{\eta}\left[\left(\frac{p_i}{p_o}\right)^2 - 1\right], \text{ whence}$$

$$\left(\frac{p_i}{p_o}\right)^2 - 1 = \frac{2\,\eta\, V_t L}{a\, K\, p_o}.$$ Substitution of this expression

for $\left(\frac{p_i}{p_o}\right)^2 - 1$ in (x) gives

$$t_g = \frac{V_g a K p_o}{3\eta V_t^2 L}\left[\left(\frac{p_i}{p_o}\right)^3 - 1\right] = \frac{V_g}{aL} \cdot \frac{a^2 K p_o}{3\eta V_t^2}\left[\left(\frac{p_i}{p_o}\right)^3 - 1\right].$$

Now $V_g = aL$, so $t_g = \frac{a^2 K p_o}{3\eta V_t^2}\left[\left(\frac{p_i}{p_o}\right)^3 - 1\right]$.

Since the speed of zone II is a constant fraction $G_g'/(G_f' + G_g')$ of the carrier speed,

$$t_e = \frac{a^2 K p_o\, [(p_i/p_o)^3 - 1]\, (G_f' + G_g')}{3\eta V_t^2 G_g'} \quad \ldots\ldots \quad \text{(xi)}$$

$$\text{and } t_e - t_b = \frac{a^2 K p_o\, [(p_L/p_o)^3 - 1]\, (G_f' + G_g')}{3\eta V_t^2 G_g'}, \quad \ldots\ldots \quad \text{(xii)}$$

where p_L = pressure at distance L_1 from outlet.

From (xi) and (xii),

$$\left(\frac{p_L}{p_o}\right)^3 = 1 + \frac{t_e - t_b}{t_e}\left[\left(\frac{p_i}{p_o}\right)^3 - 1\right]. \quad \ldots\ldots\ldots \quad \text{(xiii)}$$

Keulemans's equation (6) is

$$\frac{x}{L} = \frac{(p_i/p_o)^2 - (p/p_o)^2}{(p_i/p_o)^2 - 1},$$

where x = distance from upstream end of column to point where carrier pressure is p.

$p = p_L$ where $x = L - L_1$, so

$$\frac{L - L_1}{L} = \frac{(p_i/p_o)^2 - (p_L/p_o)^2}{(p_i/p_o)^2 - 1}.$$ Subtraction of each side of this equation from unity gives

$$\frac{L_1}{L} = \frac{(p_L/p_o)^2 - 1}{(p_i/p_o)^2 - 1} \quad \ldots\ldots\ldots\ldots \quad \text{(xiv)}$$

Equations (xiii) and (xiv) can be used to find L_1, from measured values of t_e, t_b, p_i, p_o and L.

2.5.2 <u>Method 2</u>

If $V_r^{\,o}$ is the retention volume, corrected for pressure drop, of the rear end of an ideal plateau (QR in Fig. 3), then equation (ii), p. 11, can be written $V_r^{\,o} = V_g\left(\frac{G_f'}{G_g'} + 1\right)$ and rearranged to $G_f' = G_g' \cdot \frac{V_r^{\,o} - V_g}{V_g}$. Multiply both sides of this equation by L/f:

$$\frac{LG_f'}{f} = \frac{LG_g'}{V_g} \cdot \frac{V_r^{\,o} - V_g}{f}. \quad \ldots\ldots \quad \text{(xv)}$$

LG_f'/f is obviously y; $LG_g' = \frac{P_d V_g}{RT}$, by the ideal gas law; and $\frac{V_r^{\,o} - V_g}{f}$ will be designated V_c. Equation (xv) thus becomes

$$y = \frac{P_d V_c}{RT}, \quad \ldots\ldots\ldots\ldots \quad \text{(xvi)}$$

which can be used to find y from experimental measurements.

Both Method 1 and Method 2 only yield apparent values of y if, owing to decomposition of F or any other cause, the amount of F which reacts with G is less than the amount f placed in the column and used in the calculations.

2.5.3 The application of Methods 1 and 2 to real chromatograms

The end of a real plateau is not a rectangular step as in Fig. 3, but is rounded and followed by a tail. In order to find t_e and V_r^o for use in Methods 1 and 2, it is necessary to reconstruct the ideal chromatogram from the real. This can be done by using the two facts that the ideal and real chromatograms have the same area and the same height. Let ABC in Fig. 4 be the end of a real plateau and PS its beginning. Construct rectangle PQRS to be equal in area to PABCS; then QR is the end of the ideal plateau. In Method 1, for finding the amount of G in zone II, the area PQRS (= PABCS) is taken to be the plateau area.

In many experiments in the present work, the recorder was switched off before the whole tail had been recorded. The resulting incomplete chromatograms are not suitable for area measurement, but the approximate position of QR (having retention time t_e) can be found as follows. It is easy to locate the point on the rear slope of the chromatogram that lies at half the plateau height; let the retention time of this point be t_h. For the completely recorded chromatograms obtained with a given salt-solvent system, it is usually found that t_e/t_h is approximately constant if the salt concentration does not vary widely; the average value of this ratio is used to find t_e from t_h for chromatograms lacking the complete tail.

In the calculation by Method 1 of some published[30] values of y, the rear end of the plateau was taken to be AD(Fig.4), where the chromatogram begins to drop from the plateau, and the plateau area was taken to be PADS. This approximation gives low values of y, because the part of zone II corresponding to line AD in the chromatogram originates (after passage of zone I) at some distance from the upstream end of the column. Thus the effective column length producing plateau PADS is less than the total length L, which was used in the calculations and gave too large an amount of salt in zone II.

2.6 Complexes with very low dissociation pressures

If the dissociation pressure (P_d) of $F.G_y$ is so low as to produce no detector response, the packing absorbs enough G to convert F to $F.G_y$ before G emerges at a detectable pressure. $F.G_y$ slowly decomposes in a current of carrier gas, since G is eluted at pressure P_d, and the resulting free F absorbs all or part of the next sample of G injected. If the carrier gas flows at rate V_t for time t_m between the end of chromatogram m and the beginning of the next chromatogram m + 1, the loss of G from $F.G_y$ is $P_d V_t t_m/RT$ mole, by the ideal gas equation. This loss is replenished by the G injected for chromatogram m + 1, so that the latter is produced by an effective sample of size $n-(P_d V_t t_m/RT)$ mole, where n mole is the injected sample. This effective sample size can be found from the area of chromatogram m + 1; according to equation (vii), p. 16, it is CV_tA/cRT mole. Thus

$$\frac{CV_tA}{cRT} = n - \frac{P_dV_tt_m}{RT}\text{, ----------------------------(xvii)}$$

from which P_d can be calculated.

If F and G form two complexes, of which one has a dissociation pressure too low for detection and the other produces a plateau, the effective sample size, CV_tA/cRT mole, must be used instead of the measured size, n mole, in applying Method 1 to the plateau.

A packing for which the effective sample size is less than the measured size is unsuitable for determining the calibration factor of the detector, and gives apparent values of C which are too high and vary with t_m.

2.7 Successive plateaux

If F and G form two or more complexes with detectable dissociation pressures, the chromatogram has the same number of successive plateaux, emerging in order of decreasing height, and Methods 1 and 2 can be applied to each plateau. A succession of plateaux is also given by a packing containing more than one substance forming a complex with G.

SECTION 3

APPARATUS, MATERIALS AND EXPERIMENTAL PROCEDURES

3.1 The gas-chromatographic apparatus and its operation

Fig. 5 is a block diagram of the gas-chromatographic apparatus, of which the following components were supplied by Messrs. Griffin and George, Ltd.: air thermostat, katharometer, bridge circuit and some column tubes.

3.1.1 The column

The column was a packed glass U-tube of 6.2 ± 0.2 mm internal diameter, or consisted of several such tubes joined by metal capillary tubing. Each U-tube took from 81 to 94 cm length of packing and the upstream end of the first tube was adapted to take a rubber serum-bottle cap for sample injection (see Fig. 6).

A tube was filled by pouring in the packing through a funnel and vibrating it to a compact state by holding the tube against the slightly eccentric axle of an electric motor. Each U-tube was graduated near its ends for easy measurement of the packing length. The weight of packing in a column was found by weighing the container from which the tube was filled. Packings consisting of a liquid supported on a non-porous solid did not flow freely and were pushed down the filling funnel with a glass rod; small quantities of such packings adhered to the funnel and rod, which were weighed with the container.

The volume of gas in a packing (V_g) was calculated from the column dimensions and the weights and densities of the packing constituents. (Note : If a volume V_d between the sample injector and the detector is not occupied by packing, the term V_d must be added to the right-hand side of equation (i), p. 11, and a corresponding correction to the right-hand side of

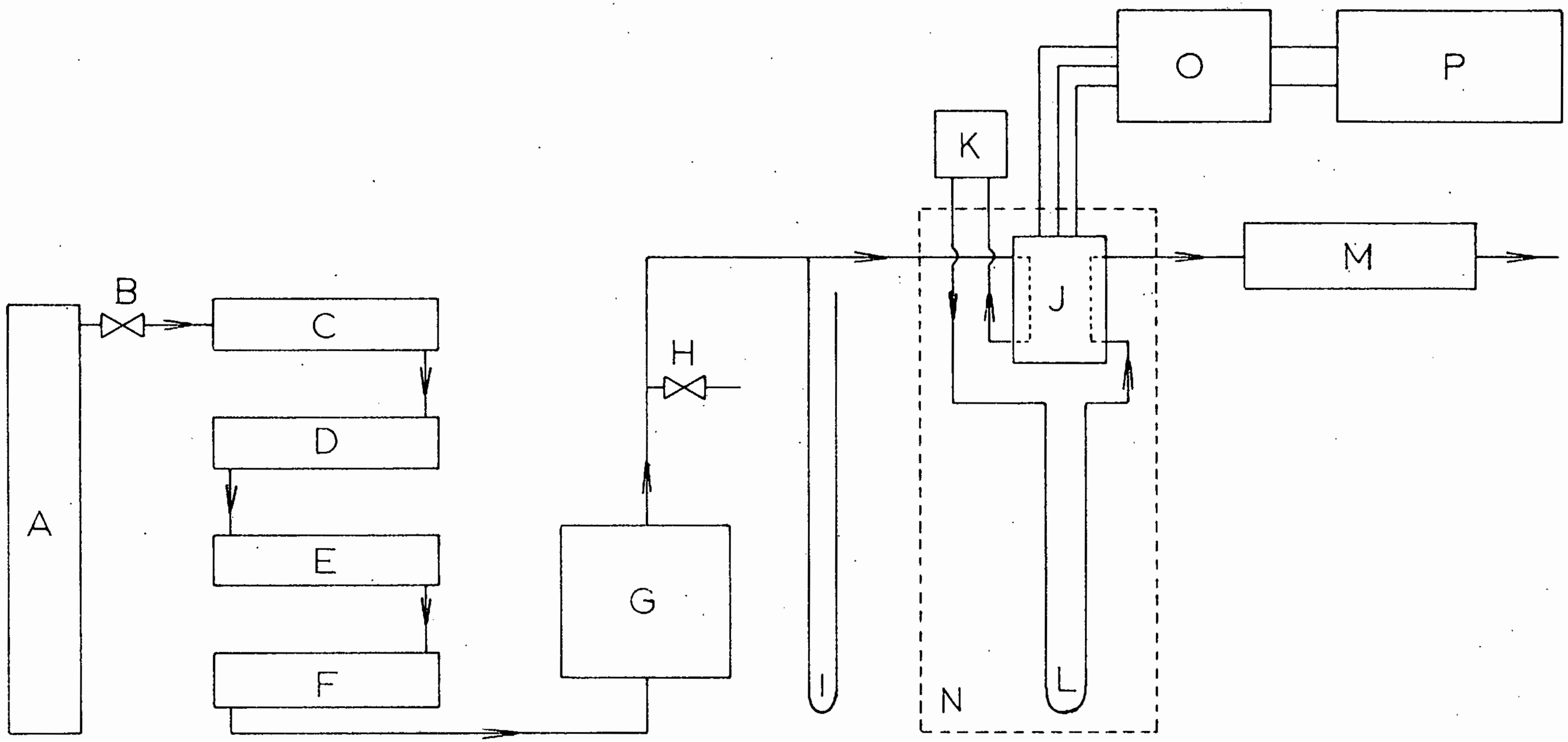

Figure 5. Block diagram of gas-chromatographic apparatus. A, gas cylinder; B, two-stage regulator; C, flow-control; D, tube containing silica gel; E, tube containing phosphorus pentoxide; F, cold trap; G, buffer vessel; H, tap to atmosphere; I, mercury manometer; J, katharometer; K, sample injector; L, column; M, flow-meter; N, air thermostat; O, bridge circuit; P, recorder.

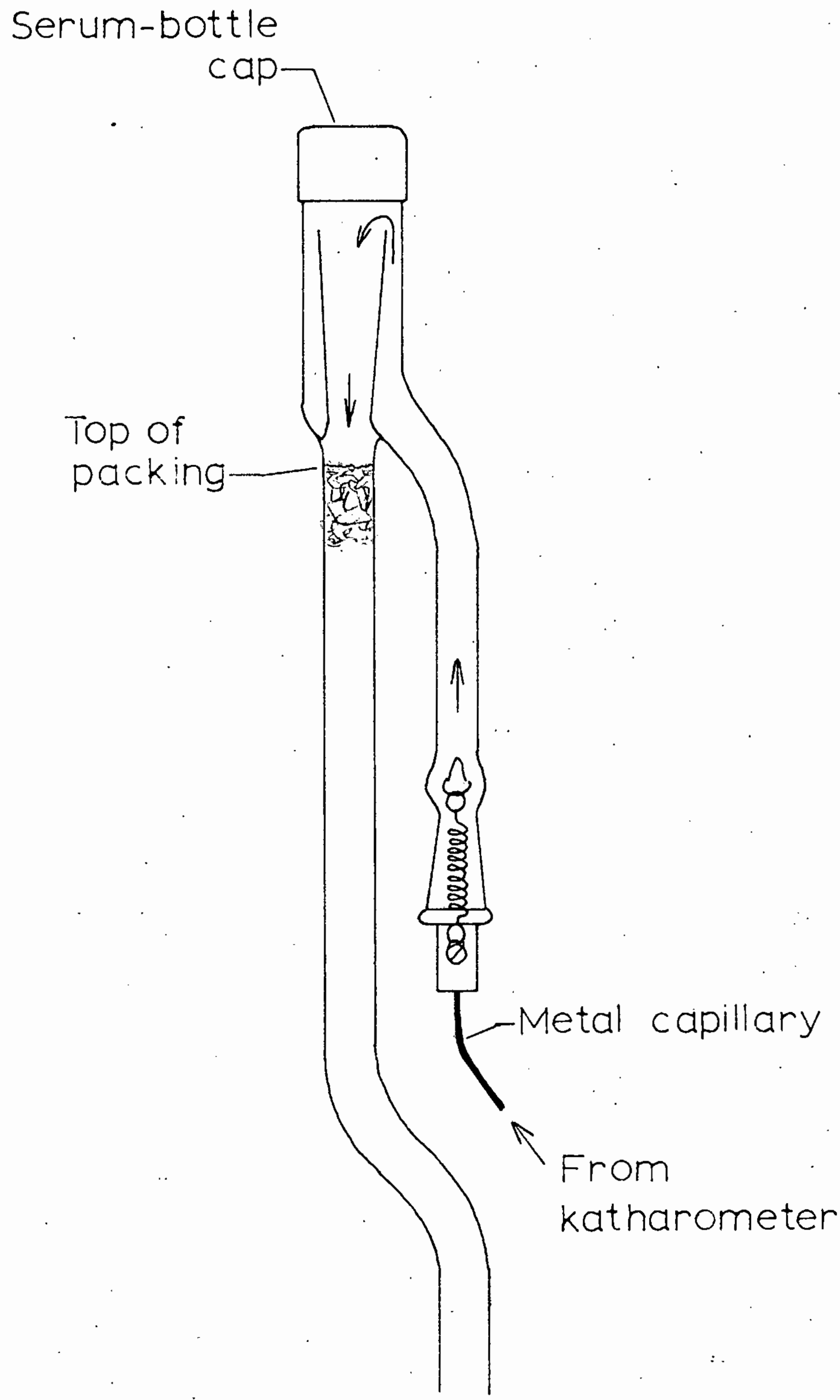

Figure 6. Top of column adapted to take serum-bottle cap. Full size. Path of carrier shown by arrows.

equation (ii), p. 11. In this work V_d is neglected, since it was kept small by the use of capillary tubing for column connections.)

Prolonged use of a column containing a liquid fixed phase resulted in the removal of the liquid by evaporation from a small length at the upstream end of the packing. Where this was observed, the denuded packing was replaced by a fresh portion.

3.1.2 The air thermostat

The column was mounted in an air thermostat of which the temperature could be set at any chosen value between about $70^\circ C$ and $180^\circ C$ and read on a mercury thermometer. The temperature remained constant to within $\pm 0.3^\circ C$ and tests with a thermocouple probe showed it to be spatially uniform to within $\pm 0.5^\circ C$ at $93^\circ C$ and $\pm 0.8^\circ C$ at $155^\circ C$.

3.1.3 The detector and recorder

The detector, a metal-block katharometer having platinum filaments in the main gas stream, was mounted in the air thermostat. Carrier gas passed from a pre-heating loop in the thermostat to the first cell of the katharometer, then via the sample injector to the column and from there to the second cell of the katharometer.

The katharometer filaments were included in a bridge circuit (Fig. 7) of which the off-balance potential was fed to a recording potentiometer. Rheostat A served to regulate the bridge current and B and C to adjust the recorder base-line, while potential divider D was used to attenuate the output.

The recorder (Honeywell-Brown Model No. 153X12V-X-6A8R) had a range of 3 mv, pen speed of $5\frac{1}{2}$ sec for full-scale travel and chart speeds of 6, 7.2, 12, 20 and 24 $in.hr^{-1}$.

3.1.4 The carrier gas

The carrier gas, usually nitrogen, was drawn from a cylinder through a two-stage regulator. Its flow-rate was controlled by means of a device described by James and Phillips[31],

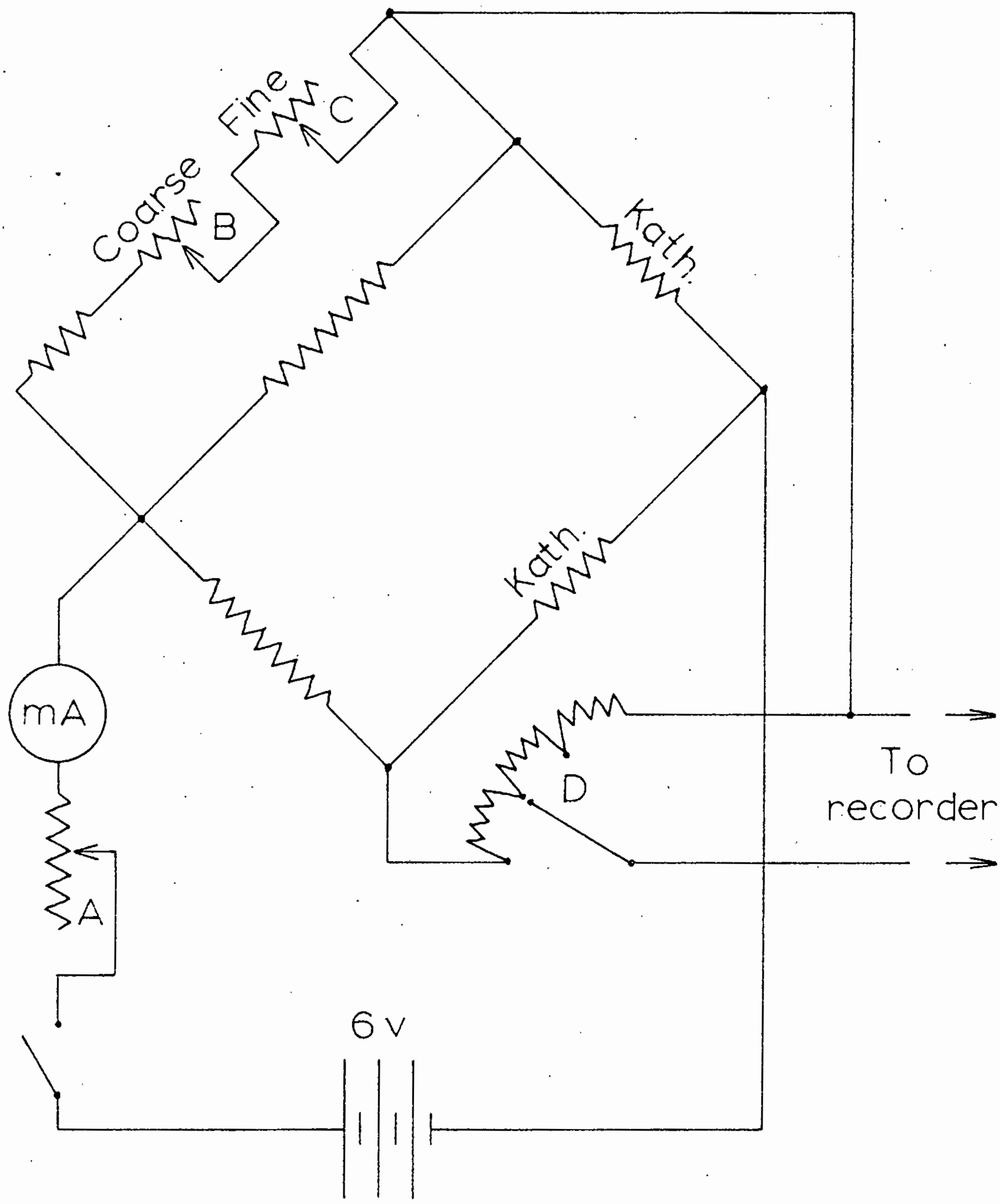

Figure 7. Detector bridge circuit. The diagram is from manufacturer's literature, which does not give the resistances of the components.

modified for high pressures as described by Littlewood, Phillips and Price [14]. Flow-rates of 6 to 120 $cm^3\ min^{-1}$ were used, the inconstancy (drift) being ± 1% at the lower of these limits and ± ½% at the upper. Oscillations of pressure due to the operation of the flow-control were smoothed out by the buffer vessel G (Fig. 5), a 4-litre bulb. The carrier gas was dried by passage over silica gel and phosphorus pentoxide and, if required very dry, by cooling trap F in liquid oxygen. Tap H was used to adjust the pressure at the column inlet, while manometer I served to measure that pressure. The flow-meter M was of the soap-film type [32] and discharged to atmosphere.

Carbon dioxide from dry ice was used for a few experiments. The dry ice was contained in a 3-litre bottle fitted with a mercury bubbler, which served as a safety-valve and could be adjusted to obtain a pressure high enough to maintain the required flow.

3.1.5 Sample injection

In the earlier work an injector using mercury, similar to that described by Harrison[33], was used. The operation of this injector and the preparation of ammonia for it were tedious, and it could not inject samples larger than 5 cm^3; these disadvantages were avoided by using a hypodermic syringe for injection, although some precision in the measurement of larger samples was thereby sacrificed.

(a) Injection by syringe

The syringes used had the following capacities and smallest graduations, cm^3 : 1,0.01; 2,0.1; 5,0.2; 10,0.5. Immediately before injection, a small quantity of ammonia was drawn into the syringe and expelled to sweep air out of the small dead volume of the nozzle and needle. The sample occupied the syringe at room temperature and atmospheric pressure, which were noted. Samples larger than 10 cm^3 were introduced by several injections in quick succession.

A punctured serum-bottle cap leaked at column inlet pressures more than 150 mm above atmospheric and for such pressures it was replaced by a rubber bung modified as shown in Fig. 8. The needle penetrated such a bung without difficulty when lubricated with silicone grease, and the punctures were sealed by the pressure of the metal band. Pressures of 450 mm above atmospheric caused no leakage.

(b) The mercury injector

Figs 9 and 10 show the injector. The volume of a portion of dry ammonia, drawn from reservoir E (Fig. 10) was measured in gas burette J, in which it was confined by mercury which could be exposed to atmospheric pressure in limb K. By raising the mercury, the measured amount of ammonia could be expelled into injector L, shown in detail in Fig. 9. Rapid and complete injection of the sample necessitated injection of some mercury into space M and this was drained through tap T_4 and returned to flask I through tap T_5. Sample volumes of 0.6 to 5 cm^3 could be measured to the nearest 0.01 cm^3. A thermometer was clamped beside the gas burette.

3.2 The preparation of ammonia

The two methods of injection required different methods of ammonia preparation.

3.2.1 Ammonia for injection by syringe

Ammonia expelled by warming from concentrated ammonia solution in flask H (Fig. 11) was dried by passage over sodium hydroxide pellets in tube G and escaped to atmosphere through mercury bubbler A. When all the air had been swept out of the apparatus, screw-clips B and E were closed and bubbler I, having a greater head of mercury than A, acted as a safety-valve for flask H. The rubber tubing was detached at F and

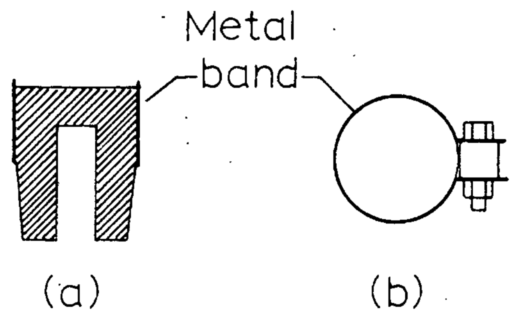

Figure 8. Modified rubber bung. Full size. (a) Section. (b) Top view.

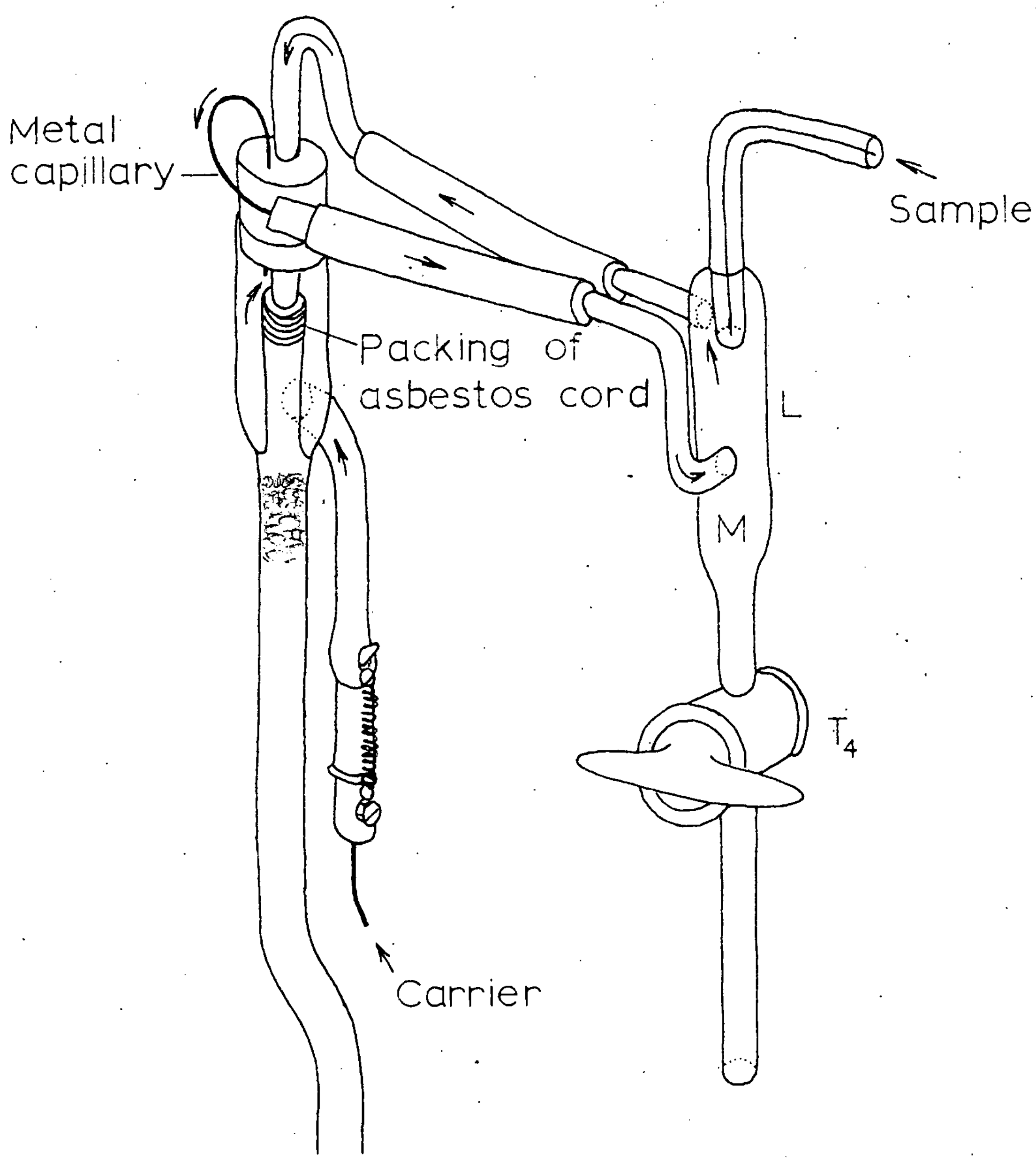

Figure 9. Mercury injector. Path of carrier shown by arrows.

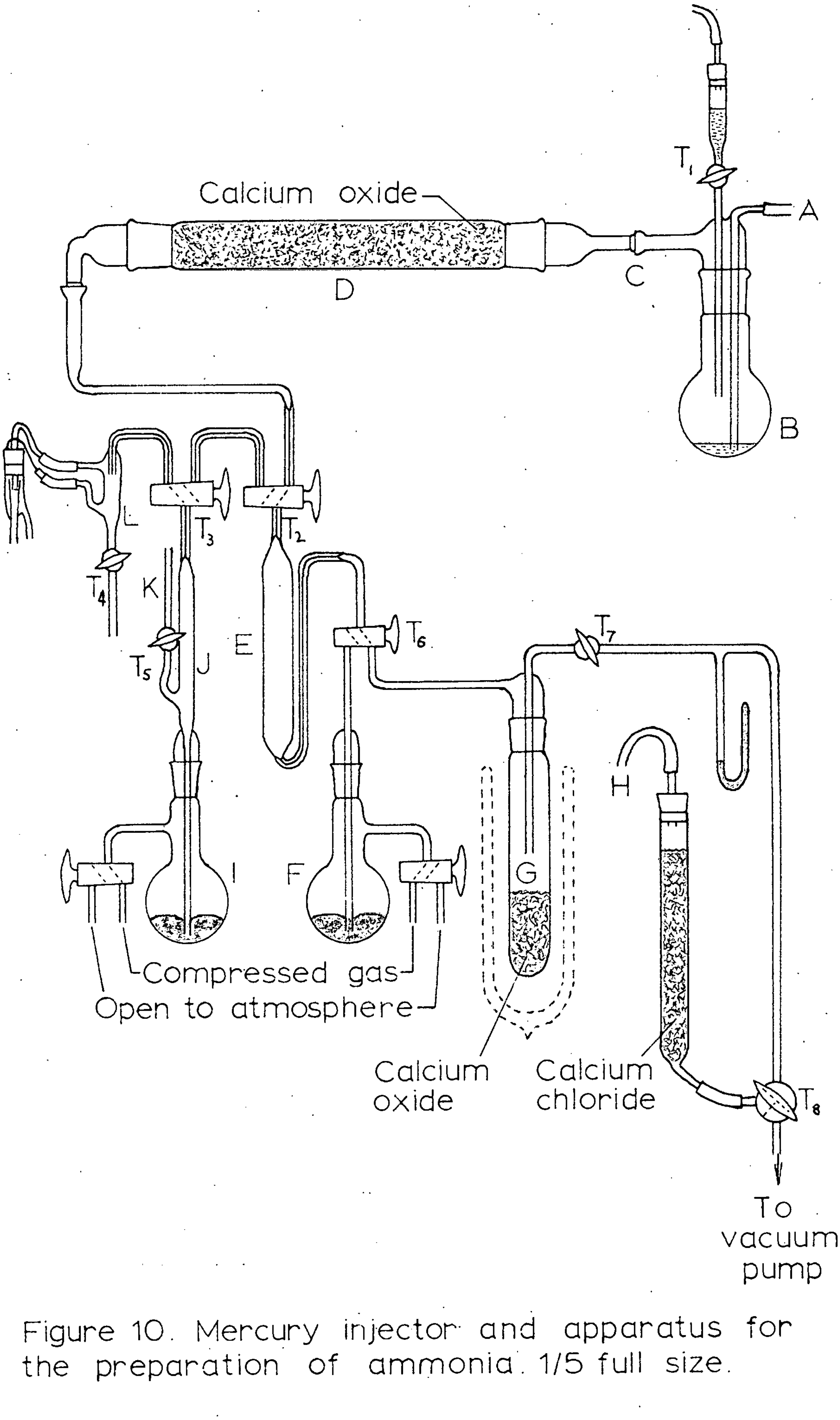

Figure 10. Mercury injector and apparatus for the preparation of ammonia. 1/5 full size.

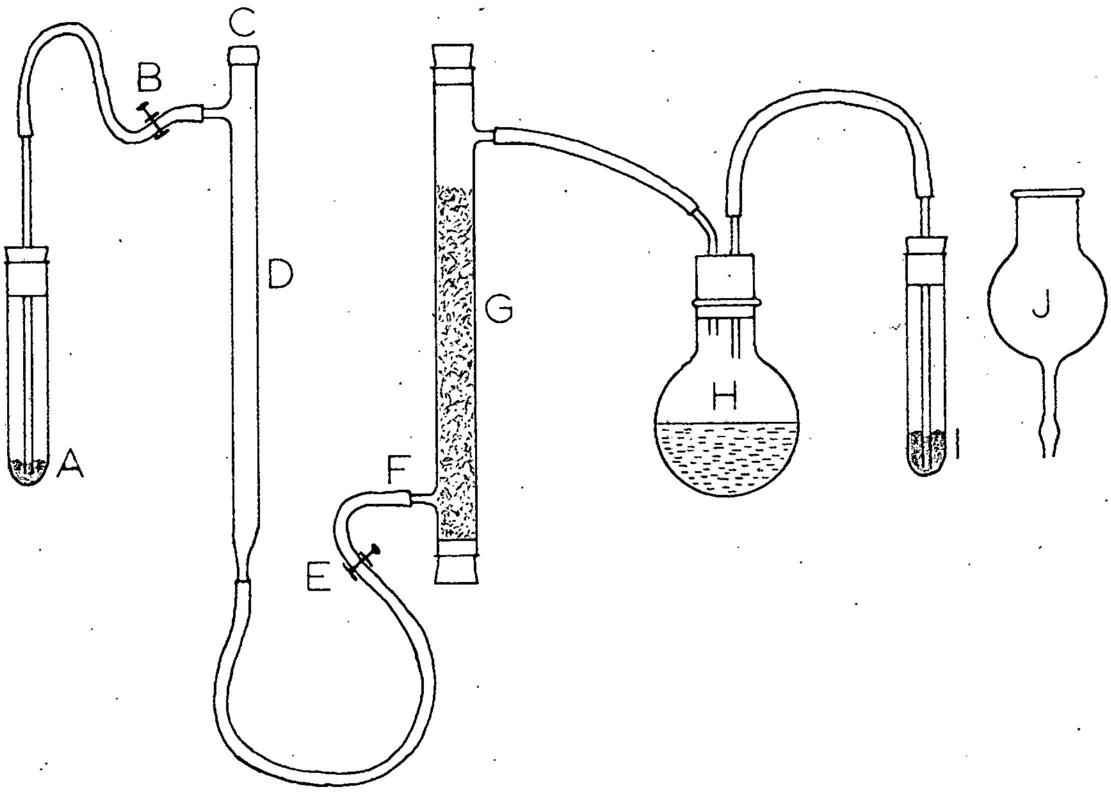

Figure 11. Apparatus for the preparation and storage of ammonia to be injected by syringe. 1/5 full size.

fitted to bulb J, which was then half-filled with mercury. Screw-clip E was opened and the mercury ran down the rubber tube and served to manipulate the ammonia in tube D, from which the syringe was filled through the serum-bottle cap C. Gas chromatography showed that the ammonia so prepared sometimes contained traces of impurities.

3.2.2 Ammonia for the mercury injector

The stock of ammonia in reservoir E (Fig. 10) was prepared as follows. A suitable amount of ammonium nitrate was weighed into flask B and dissolved in the minimum amount of water. The mercury in flask F was raised to fill the bore of tap T_6, and that in flask I raised through tap T_3 to fill the bore of T_2. Taps T_2, T_6, T_7 and T_8 were turned to provide an open passage from point A to point H; trap G, containing calcium oxide, was cooled in liquid oxygen, concentrated sodium hydroxide solution introduced through tap T_1, and nitrogen bubbled through the liquid in flask B at about 1 litre min^{-1} to sweep the ammonia evolved through the calcium oxide desiccant in tube D to trap G, where it solidified. The passage of nitrogen was continued for $\frac{1}{2}$ hr, with gentle warming of flask B towards the end of this period. Tap T_2 was then closed and the apparatus evacuated through tap T_8 up to tap T_2. Taps T_6 and T_7 were closed, the liquid oxygen removed from trap G and about a day allowed for the calcium oxide to absorb the small quantity of water detained with the ammonia. Then reservoir E was cooled in liquid oxygen and tap T_6 opened to connect it to trap G. Several hours were allowed for the ammonia to condense in reservoir E, tap T_6 was closed, the liquid oxygen removed and mercury raised through tap T_6 to confine the ammonia in the reservoir. Gas chromatography showed that ammonia so prepared sometimes contained traces of impurities.

3.2.3 Explosion Danger

Mercury and ammonia react in the presence of iron and moisture or air to form an explosive compound[34]. It is reported[35] that pure mercury and pure ammonia in glass vessels do not react, so that the apparatus here described seems to be safe.

3.3 The preparation of packings

Most of the work was done with solutions of silver salts supported on fine glass beads (0.1 mm diameter). In earlier experiments, the solution was diluted with a volatile solvent and made into a slurry with the beads, after which the volatile solvent was evaporated with agitation of the slurry to leave a uniform coating on the beads. Later it was found that thorough shaking coated the beads effectively, and the volatile solvent was dispensed with. For the preparation of the solutions used as fixed phases, the solvent volumes were measured with pipettes calibrated for water, and small differences in delivery due to viscosity differences were neglected.

A few solid fixed phases were tested; they were prepared by crushing the solids and screening to the required particle size, these operations being performed as quickly as possible for hygroscopic salts. The lead halides were available only as fine powders, and were first consolidated to lump form by moistening and baking.

Details of the preparation of individual packings are given in Section 4.

3.3.1 Materials used

Table 1 shows the origin, purity and other specifications of the materials used for preparing packings. For most silver-salt packings the solvents were purified by distillation at reduced pressure.

Table 1 Materials used for packings

Substance or material	Manufacturer	Grade or manufacturer's description	Specifications
Benzonitrile	British Drug Houses	Laboratory Reagent	-
Benzyl cyanide	British Drug Houses	Laboratory Reagent	-
Calcium chloride	British Drug Houses	Laboratory Reagent	Assay, ex Cl, $\nless$ 90%
Charcoal	Merck	Blocks for blow-pipe analysis	-
Copper, granular	British Drug Houses	Laboratory Reagent	-
Ethyl ether	Riedel-de Haën	Analytical Quality	-
Fenchone	Kodak	Technical	-
Firebrick, crushed	Sterchamolwerke	Backfilling material	0.2 - 0.4 mm diam.
Glass beads	English Glass Co.	"Ballotini", grade 15	0.1 mm diam.
		"Ballotini", grade 8a	0.4 mm diam.
Lead bromide	British Drug Houses	Laboratory Reagent	-
Lead chloride	British Drug Houses	Laboratory Reagent	-
Tetralin	L. Light and Co.	Purified	-
	Riedel-de Haën	-	-
m-Toluidine	L. Light and Co.	Purified	-
Silver nitrate	May and Baker	Laboratory Chemical	$\nless$ 99.8%
	Hopkin and Williams	Analar	$\nless$ 99.9%
Zinc dialkyldithiophosphate	American Cyanamid Co.	"Accolube 93 C"	80% zinc dialkyldithiophosphate, 20% mineral oil (92% Zn)

3.3.2 The preparation of soaps

Heavy-metal soaps were prepared by double decomposition of sodium soaps and heavy-metal salts in aqueous solution. Copper oleate, for instance, was obtained by dissolving a known weight of sodium oleate in water and adding a solution of somewhat more than the equivalent amount of copper sulphate. The resulting precipitate of copper oleate was washed with water till the washings gave no precipitate with barium chloride solution, and then dried on a steam bath. Other soaps were prepared by similar procedures, the products being hydrated to an unknown degree.

3.3.3 The preparation of silver perchlorate

Silver perchlorate was prepared by adding silver carbonate to a few millilitres of 60% perchloric acid till a little remained undissolved. The solution was filtered, acidified with a drop of perchloric acid to prevent possible decomposition and evaporated nearly to dryness. The residue of moist monohydrate was transferred to a weighing bottle which was placed, without its lid, in the copper bucket shown in Fig. 12. Three hours of evacuation and warming (110°C) rendered the salt anhydrous (found : Ag, 52.0%; Ag ClO_4 requires Ag, 52.1%). The bucket facilitated rapid transfer of the weighing bottle from the dehydrating tube to a desiccator. A weighing bottle with a female lid was used to avoid fouling of the ground joint by silver perchlorate being tipped out for weighing.

3.4 The tensimeter

The tensimeter shown in Fig. 13 was used in a thermostatted room with a thermometer mounted near tube A. Its volume was found as a function of the mercury level in the manometer by introducing measured volumes of water. A known weight and volume of ammine-forming material was placed in

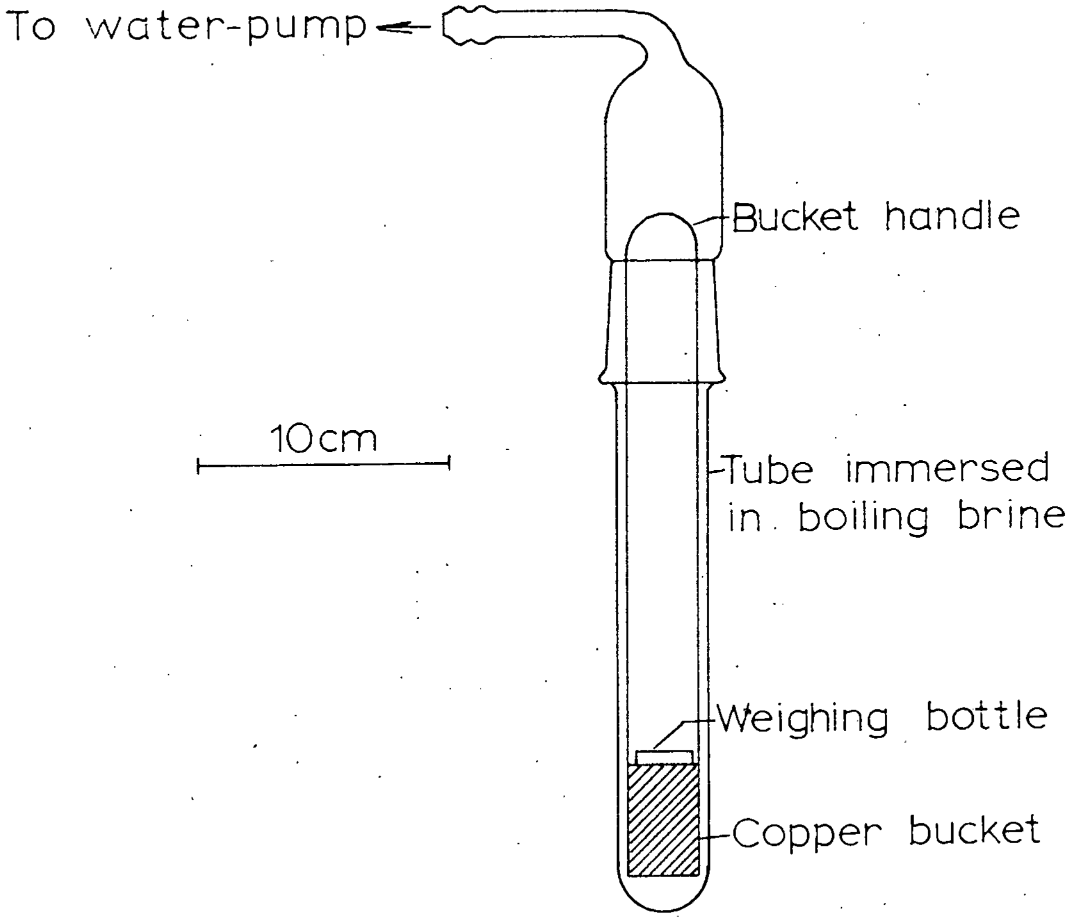

Figure 12. Dehydrating tube.

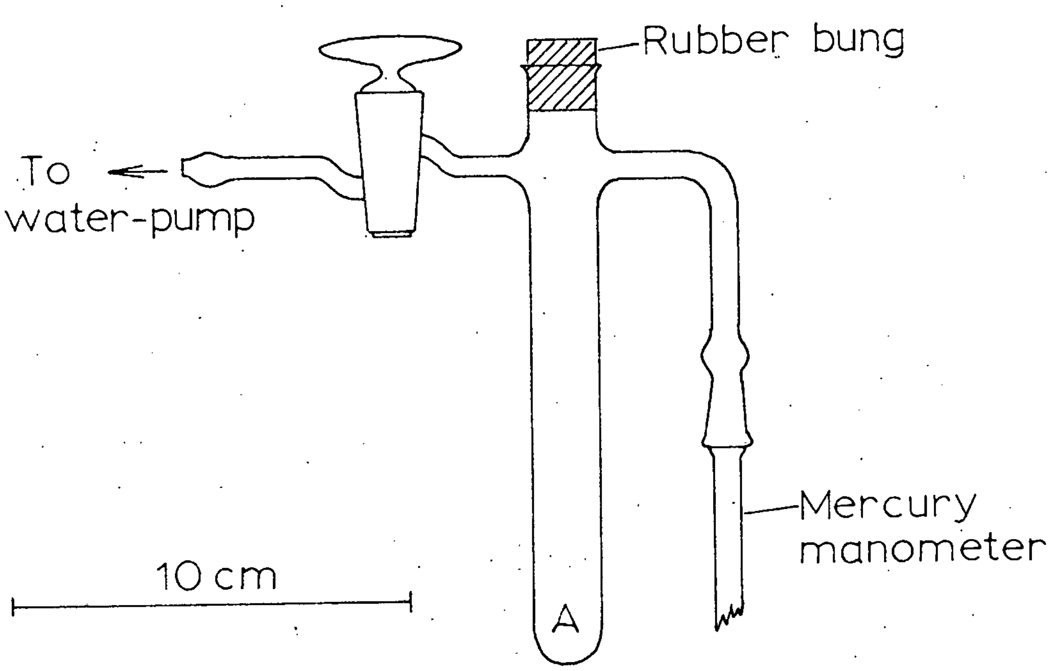

Figure 13. Tensimeter.

tube A, the latter was partly evacuated and the tap closed. The volume, pressure and temperature of the residual air were noted and a known amount of ammonia was injected by syringe through the bung. When the manometer had become steady, the pressure and volume of the gases and the temperature were again noted and used to calculate the pressure and amount of ammonia remaining in the gas phase and, by difference, the amount absorbed by the ammine. Successive injections of ammonia gave points on a graph of ammonia pressure against amount absorbed.

SECTION 4

EXPERIMENTAL RESULTS

This section presents the experimental results obtained and their interpretation. The first sub-section explains the presentation of data; the second and third describe the preliminary search for a solid support and tests on the solvents used in fixed phases. Then follows the main part of the work in a series of sub-sections of which each is devoted to one salt-solvent system. Finally, some miscellaneous earlier results are reported.

4.1 The presentation of data

Tables of certain data occur repeatedly in 4.4 to 4.14 and are generally drawn up according to the following three schemes :

Tables showing characteristics of packings

Column 1. Designation of packing. The first letter indicates the solute (N for silver nitrate, P for silver perchlorate); succeeding letters indicate the solvent (BC for benzyl cyanide, BN for benzonitrile, F for fenchone, T for tetralin, X for mixtures of benzonitrile and m-toluidine).

Column 2. Concentration of silver salt in solution acting as fixed phase.

Column 3. Ratio (s) of fixed phase to support.

Tables of experimental conditions and results

Column 1. Experiment number. Each experiment is given a number for reference in the text, figures and other tables.

Column 2. Carrier flow-rate. Expressed as flow-rate of dry gas (i.e. corrected for water vapour from flowmeter) at atmospheric pressure and column temperature.

Column 3. Sample size. Expressed in μmole for convenient comparison with amount of salt in column.

Column 4. Column temperature.

Column 5. Dissociation pressure (P_d) of ammine responsible for plateau. Calculated from calibration factor, $C = 2.2(3) \times 10^{-3}$ atm cm^{-1} (4.14.4, p.115). Pressures are designated as explained in 5.1, p.129 .

Column 6. V_c for end of plateau, calculated from approximate value of t_e, found as described in second paragraph of 2.5.3, p. 21 .

Column 7. y calculated by Method 2 from V_c in column 6.

Tables of this kind are divided into sections for different gas-chromatographic columns, each section being headed by the packing designation, packing length, amount of silver salt in column and linear concentration of silver salt.

<u>Tables comparing Methods 1 and 2</u>

Column 1. Experiment number.

Column 2. Calibration factor.

Column 3. y by Method 1, from measured sample size.

Column 4. y by Method 1, from effective sample size calculated by equation (vii), p. 16 .

Column 5. t_e/t_h (see 2.5.3, p. 21).

Column 6. y by Method 2, from reconstructed ideal plateau (see 2.5.3, p. 21).

Column 7. Approximate value of y by Method 2, from average value of t_e/t_h (see 2.5.3, p. 21).

These schemes of tabulation are not used in 4.2, 4.3, 4.15, 4.16 and 4.17, but data in these sub-sections are expressed as described in the schemes.

Except where otherwise stated, the carrier gas was nitrogen dried with phosphoric oxide, and the bridge current was 150 ma.

4.2 The solid support

The solid support in gas-liquid chromatography should (i) have a large surface area over which the liquid phase can be spread in a thin layer; (ii) have a large particle size, so as to present little resistance to gas flow; (iii) not be a strong adsorbent for the substances being chromatographed, since retention by the support is superimposed on that due to the liquid phase. Requirements (i) and (ii) are compatible only when the solid is porous, so that surface area is little affected by changes in particle size. For the chromatography of highly polar substances like ammonia, it is particularly important that the solid support should be a weak adsorbent.

4.2.1 Materials tested for their suitability as solid supports in the chromatography of ammonia

Crushed fire-brick, a porous solid of large particle size, is widely used as a support. The following fire-brick packings were tested, some of them after treatment with alkali to reduce their affinity for ammonia.

B1. Washed with water to remove dust, dried at 200°C for 6 hr.

B2. Washed with water to remove dust, impregnated with 5% aqueous sodium hydroxide, dried at 200-230°C for 3 hr.

B3. Impregnated with 10% aqueous sodium hydroxide, washed 7 times with water (carbon dioxide bubbled through at 6th washing; neutral to litmus at 7th washing), dried at 200-225°C for 6 hr.

Fine glass beads have been used in gas-solid chromatography as a weak adsorbent[1,2] and were tested, after various treatments, for low adsorption of ammonia.

G1. 0.1 mm diam. No preliminary treatment.

G2. 0.1 mm diam. Washed 5 times with distilled water, dried at 200-220° C.

G3. 0.1 mm diam. Treated with dilute hydrochloric acid (unknown strength), washed well with water, dried in oven.

G4. 0.1 mm diam. Simmered gently for ½ min. with 30% aqueous sodium hydroxide, washed with water till neutral to litmus, dried in oven.

G5. 0.1 mm diam. Boiled vigorously for 2 min. with 30% aqueous sodium hydroxide, washed with water till neutral to litmus, dried in oven.

G6. 0.1 mm diam. Same treatment as G5.

G7. 0.4 mm diam. No preliminary treatment.

G8. 0.4 mm diam. Same treatment as G5.

Particles of granular copper are very irregular in shape, and therefore have a larger surface area than glass beads of the same mesh size. A packing of 36-60 mesh was tested.

4.2.2 Results of tests on supports

The packings described in 4.2.1 were not tested in a planned series of experiments with standardized operating conditions, and the results obtained (Table 2) can therefore be only roughly compared. Tailing of the peaks (see 2.2.2, p.12) occurred in all cases.

Table 2 Results of tests on supports

Packing	Column length cm	Flow-rate $cm^3\ min^{-1}$	Sample µmole	Column temp. deg C	V_r^o for peak maximum cm^3	Peak height cm	Bridge current ma	Pressure drop mm
B1	96.0	101.(3)	95	18.7	92(0)	0.50*	120+	(210)×
B2	82.0	108.(3)	203	20.7	4(5)	>26.55†	150	58
B3	88.3	109.(3)	200	22.1	10(4)	7.80	150	64
G1	93.4	29.6	129	24.0	275	1.13*	150	237
G2	89.2	39.6	73	17.6	241	1.64*	150	314
G3	90.0	41.5	72	17.1	33	10.38*	150	297
G4	92.9	37.5	37	22.1	28	15.90	150	324
G5	92.7	40.2	37	22.0	23	>26.52†	150	374
G6	91.4	9.6(8)	38	18.3	18	30.10	150	103
G6	91.4	9.6(8)	$1cm^3$ air	18.3	16	-	150	103
G7	90.0	38.1	38	21.0	16	>26.04†	150	25.0
G8	90.0	38.5	38	21.0	16	>26.81†	150	26.4
Copper	95.7	99.(5)	107	19.3	4(1)	11.83*	120+	199

* Obtained with an uncalibrated katharometer of sensitivity similar to that of the calibrated one.

\+ Recorder deflection at 120 ma about 75% of that at 150 ma.

× Capillary connection to injector blocked. Pressure drop of 60 mm assumed for calculation of V_r^o.

† Peaks off-scale.

Fire-brick untreated with alkali (B1) is too retentive to be useful as a support. Impregnation with sodium hydroxide (B2) reduces ammonia retention markedly, but is objectionable when the fixed phase contains a salt which may react with the alkali. Removal of the sodium hydroxide by washing and neutralization with carbon dioxide (B3) produces a moderate increase in retentivity, but this may be tolerable when the porosity of the fire-brick and its low resistance to gas flow are important (long column and high liquid/support ratio).

The finer glass beads (0.1 mm diam.) are very retentive when untreated (G1) or washed with water only (G2), but are much improved by treatment with hydrochloric acid (G3) or sodium hydroxide solution (G4, G5, G6). The latter produces its full effect only when boiled vigorously (compare G4 and G5). Comparison of the two results for G6 shows that the ammonia-peak maximum travels with nearly the speed of the carrier over alkali-treated beads. The coarser beads (0.4 mm diam) require no treatment (compare G7 and G8) and offer much less resistance to gas flow (compare G8 and G2) but because of their small specific area are suitable only for packings with a low liquid/support ratio.

The granular copper is non-retentive and permeable enough to be used as a support.

Of the possible supports, those selected for use were the copper, coarse glass beads and fine beads treated with sodium hydroxide. In all the packings described in 4.3 to 4.14 the support was fine glass beads boiled with 30% aqueous sodium hydroxide, washed and dried.

4.3 <u>The solvents used in packings containing silver salts</u>

The experiments described in 4.4 to 4.14 were carried out with packings containing silver salts dissolved in benzyl cyanide, benzonitrile, fenchone, tetralin and m-toluidine. To estimate their affinity for ammonia, these liquids were tested in packings resembling those of 4.4 to 4.14 but containing no silver salt.

Each packing was made by coating 50.00 g of glass beads with 1.50 cm^3 of the redistilled liquid. Experimental conditions were as follows :

Packing weight, g	47.39 - 48.65
Packing length, cm	92.2 - 94.8
Carrier flow-rate, $cm^3\ min^{-1}$	9.6(0) - 9.9(8)
Column temperature	17.2° - 17.6° C for m-toluidine
	21.1° - 22.4° C for other liquids.

The retention volume of the peak maximum per unit volume of fixed phase, $(V_r^{\circ} - V_g)/V_f$, is useful for comparing different solvents and is recorded in Table 3. (When adsorption is negligible, which is not the case here, $(V_r^{\circ} - V_g)/V_f$ is the partition coefficient. See equation (iv), p. 11 .)

Table 3. Retention volumes of solvents*

Sample µmole	Benzyl cyanide	Benzonitrile	Fenchone	Tetralin	m-Toluidine
78 - 80	16.(4)	17.(9)	10.(4)	26.(5)	44.(7)
37 - 38	18.(2)	19.(7)	11.(8)	35.(3)	45.(9)
17	20.(0)	21.(4)	12.(9)	44.(3)	47.(6)

* Values for m-toluidine are single determinations; those for the other solvents are averages of duplicate determinations differing by not more than 0.6.

In all cases, $(V_r^{\circ} - V_g)/V_f$ increases with decrease in sample size, in accordance with the observation that the peaks showed tailing (see 2.2.2, p. 12). The increases in $(V_r^{\circ} - V_g)/V_f$ from largest to smallest sample are similar in magnitude for benzyl cyanide [3.(6)], benzonitrile [3.(5)], fenchone [2.(5)] and m-toluidine [2.(9)], and are probably due to adsorption on the support. For tetralin, however, the increase is much larger [17.(8)], and indicates that the partition coefficient decreases with increase in ammonia concentration, i.e. Henry's law is not obeyed. The high solubility of ammonia in m-toluidine may be due to hydrogen bonding between the nitrogen atoms of the two compounds.

Since glass beads are not absorbent, packings made by coating them with liquid are not free-flowing and cannot be packed perfectly uniformly. Small variations in column diameter also contribute to non-uniformity of the linear packing density.

For the packings and experimental conditions described in 4.3 to 4.14, the pressure drop is about 0.03 mm per cm column length and per unit flow-rate ($cm^3\ min^{-1}$), corresponding to a packing permeability of $2 \times 10^{-7}\ cm^2$.

4.4 Silver nitrate in benzyl cyanide

Solutions of silver nitrate in benzyl cyanide have been used for the gas-chromatographic separation of olefins[36]. Experiments in the chromatography of ammonia on such solutions led to the discovery of plateau chromatograms.

A new packing absorbs some ammonia (see 2.6, p.22) and then, under suitable conditions, gives chromatograms having two plateaux. A slow ageing process is evident in chromatograms obtained over a long period, particularly with a packing containing a concentrated solution.

Ammonia reacts with silver nitrate in benzyl cyanide to form a white precipitate, so that such a solution behaves as a heterogeneous fixed phase.

4.4.1 The packings

In the preparation of the earlier packings, dry ethyl ether was used as a volatile solvent (see 3.3, p.35) and evaporated in a stream of dry nitrogen. Addition of ether to the more concentrated solutions (~70 μmole cm^{-3}) caused some precipitation of the silver nitrate.

Table 4 shows the characteristics of the packings used.

Table 4   Packings containing silver nitrate in benzyl cyanide

Packing	Concentration μmole cm^{-3}	10^2 s cm^3 g^{-1}	Silver nitrate, manufacturer	Benzyl cyanide re-distilled	Ether used
NBC1	24.4	3.33	M & B	No	Yes
NBC2	46.9	3.33	M & B	No	Yes
NBC3	63.3	3.03	M & B	No	Yes
NBC4	70.1	3.33	M & B	No	Yes
NBC5	93.(3)	3.60	H & W	Yes	No
NBC6	394	3.00	H & W	Yes	No
NBC7	395	3.00	H & W	Yes	No
NBC8	396	3.00	H & W	Yes	No

The packings turned pale mauve soon after preparation, before injection of ammonia, but showed no further colour change.

4.4.2 The initial absorption

The following values of the initial absorption (moles of ammonia per mole of silver nitrate) were found :

Packing NBC5 1.4

Packing NBC7 $\ngtr$ 1.8

Packing NBC8 1.7

Further slight absorption may occur during the ageing described in 4.4.6, p.59 , but was not detected.

4.4.3 The lower plateau

When the initial absorption has taken place, samples below a certain size produce chromatograms showing one plateau only, the lower of the two in Fig. 18.

After preliminary experiments with Packing NBC3, Packings NBC1, NBC2 and NBC4 were prepared to investigate the effect of changes in sample size, column length and silver nitrate concentration. Tests on the leaner packings NBC1 and NBC2 were started within a day of their preparation, but NBC3 and NBC4 were found to give ill-defined plateaux immediately after preparation. It seemed possible that this might be due to slow re-solution of silver nitrate precipitated by the ether used as a volatile solvent, but it was later found that packings prepared without ether also change on ageing (4.4.6, p.59); the columns were allowed to age for a week, after which they gave definite plateaux and showed no further change during the time of their use.

Figs. 14-17 show a selection of chromatograms illustrating the influence of the variables studied, the results being in accordance with the predictions made in the last paragraph of 2.3.1, p.15 . A low peak results from a sample too small to produce a plateau (Fig. 14, Expt. 6).

Some details of the chromatograms call for comment. Injection is always marked by a vertical line (A, Fig. 14, Expt. 13) caused by the pressure disturbance. In some of the chromatograms, one or two small positive peaks (C, Fig. 14, Expt. 13) precede the ammonia peak and these are ascribed to traces of impurities in the ammonia, which was introduced with the mercury injector. The small negative peak B (Fig. 14, Expt. 13) always starts immediately after injection, irrespective of column length, and its area decreases with increasing salt concentration (12, 9, 6 mm^2 for Expts. 13, 22, 52, Fig. 16); it may be due to diffusion of ammonia into the upstream cell of the katharometer, and an increase in salt concentration may perhaps reduce such diffusion by more rapid removal of the sample from the gas space upstream from the packing. The chromatograms of Fig. 18 were obtained with larger samples (injected by syringe) than those used for the chromatograms shown in Figs. 14-17; injection is marked by a negative deflection, followed by a gradual return to the base-line. This is ascribed to a surge of the sample into the upstream cell of the katharometer.

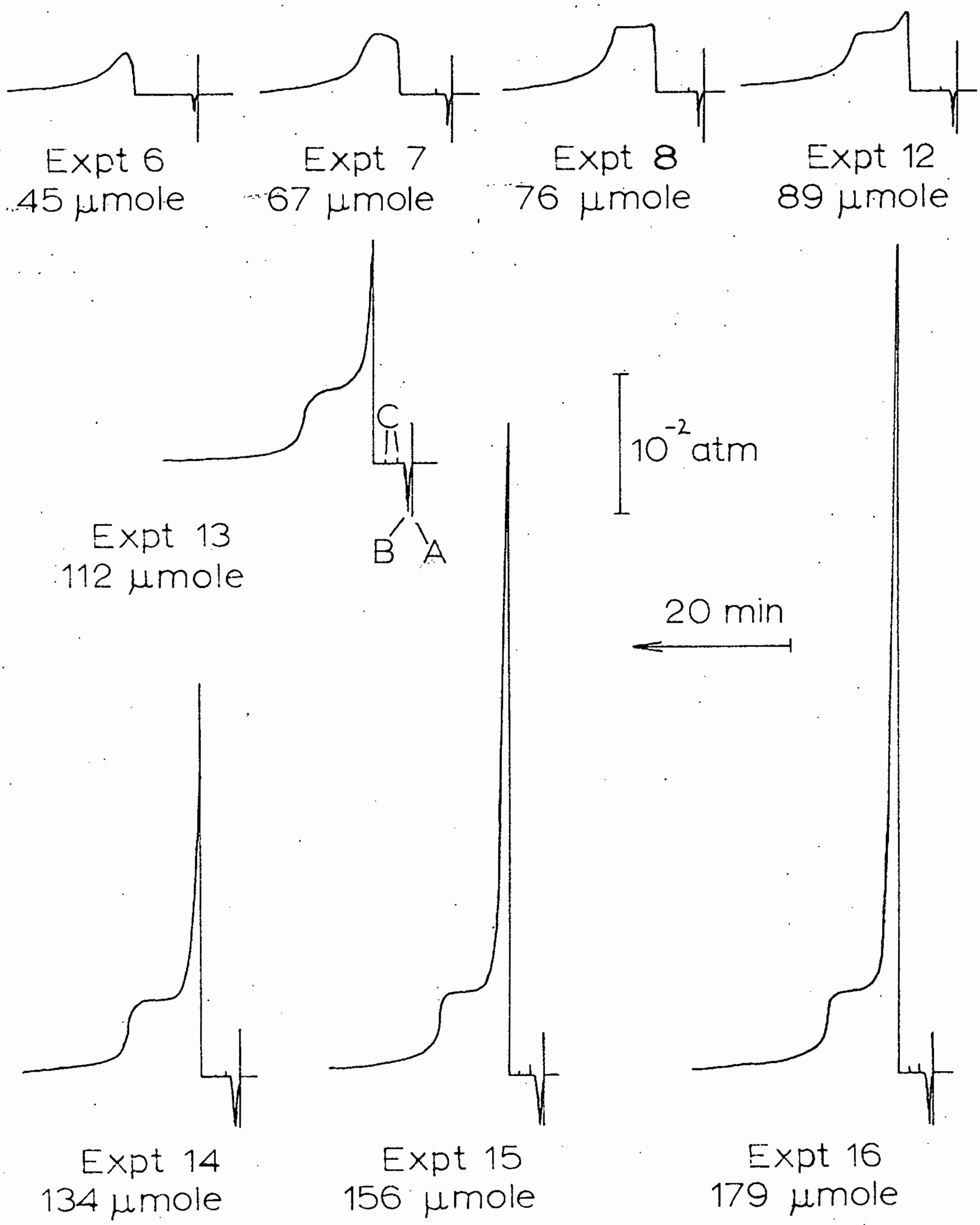

Figure 14. Silver nitrate in benzyl cyanide—effect of sample size. Packing NBC1, column length 254.0 cm, flow-rate 34.3-34.8 $cm^3 min^{-1}$, column temp. 17.4-19.8°C.

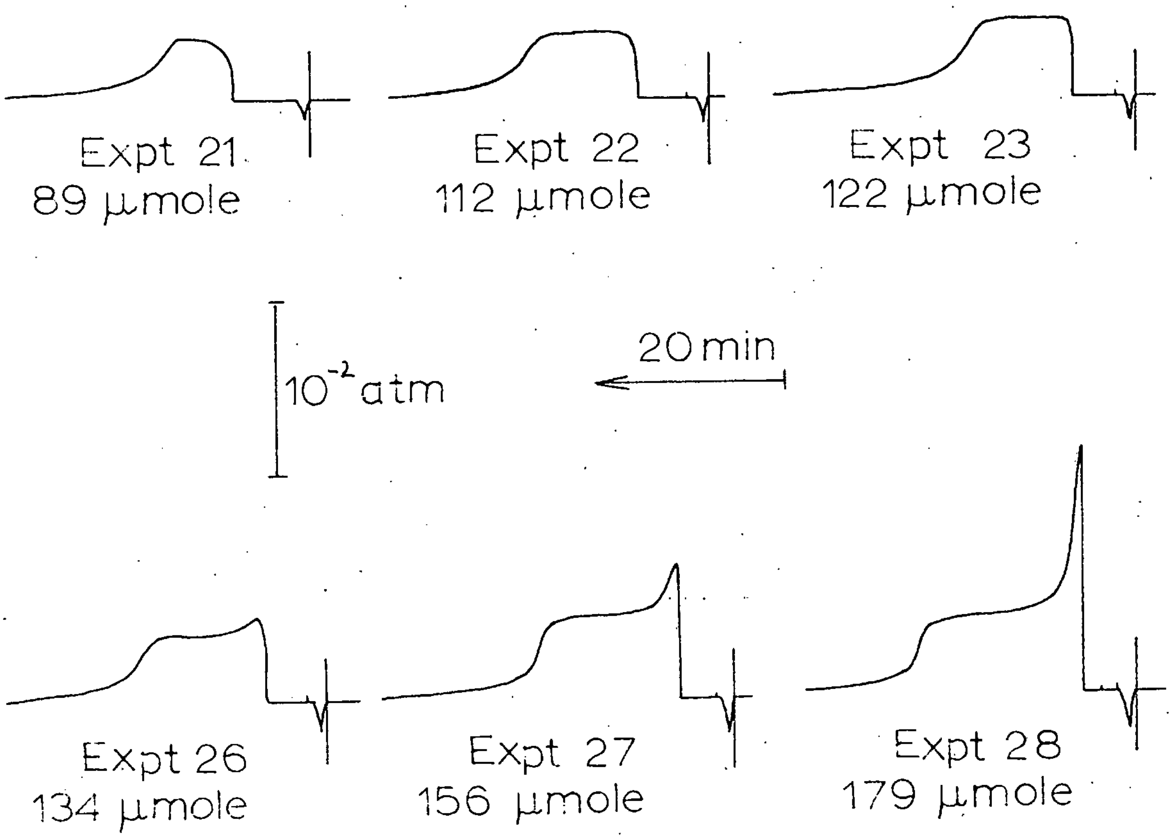

Figure 15. Silver nitrate in benzyl cyanide—effect of sample size. Packing NBC2, column length 254.0 cm, flow-rate 33.8-34.8 $cm^3 min^{-1}$, column temp. 18.2-20.1°C.

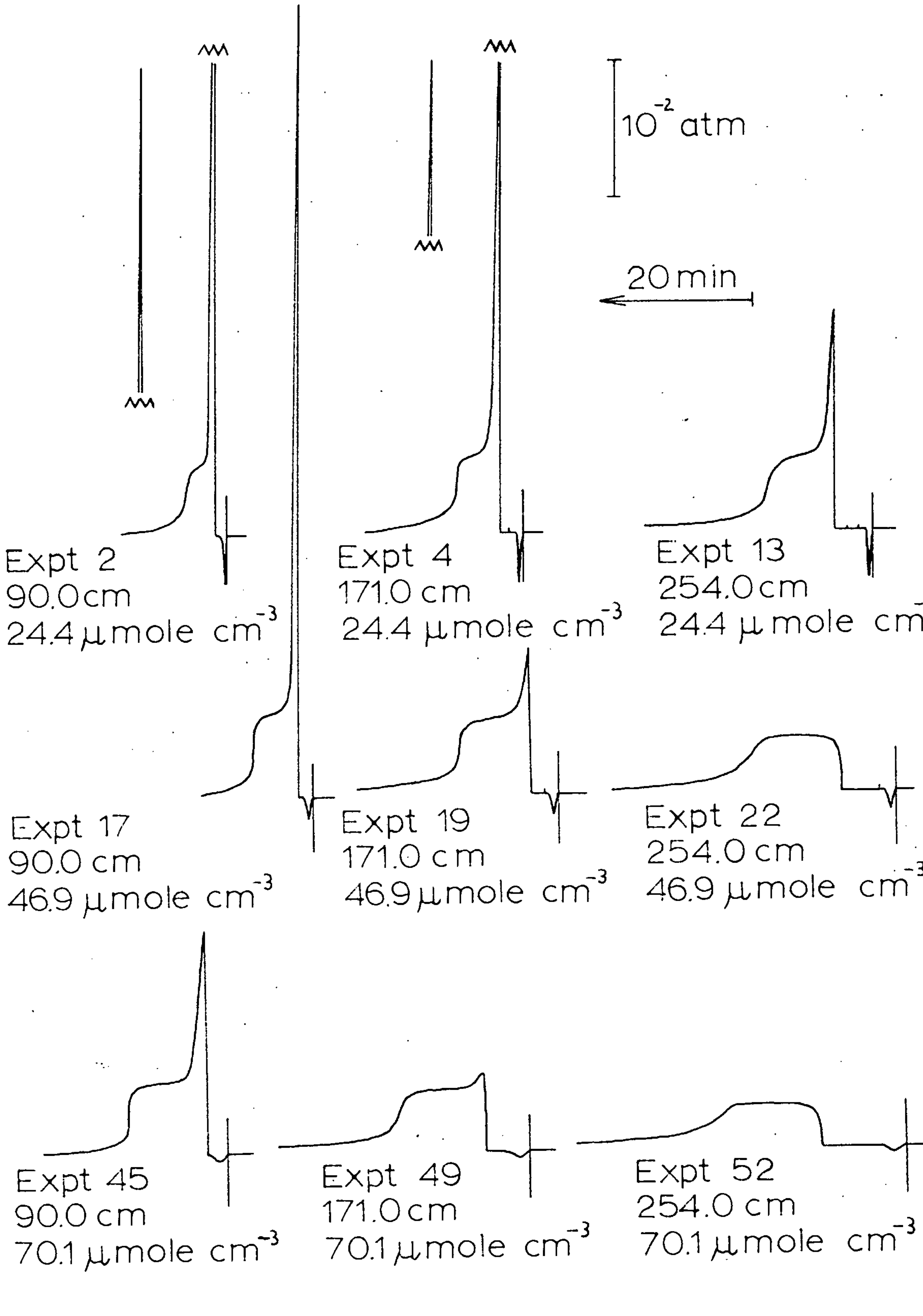

Figure 16. Silver nitrate in benzyl cyanide—effect of column length and silver nitrate concentration. Flow-rate 34.1-34.8 cm^3 min^{-1}, sample 112 μmole, column temp. 17.7-20.7°C.

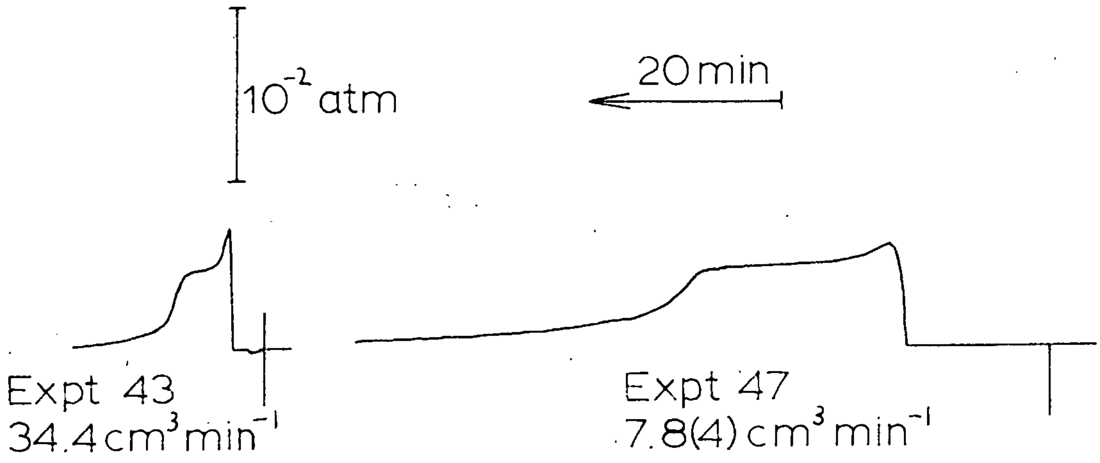

Figure 17. Silver nitrate in benzyl cyanide — effect of carrier flow-rate. Packing NBC4, column length 90.0 cm, sample 68 μmole, column temp. 20.1-20.6°C.

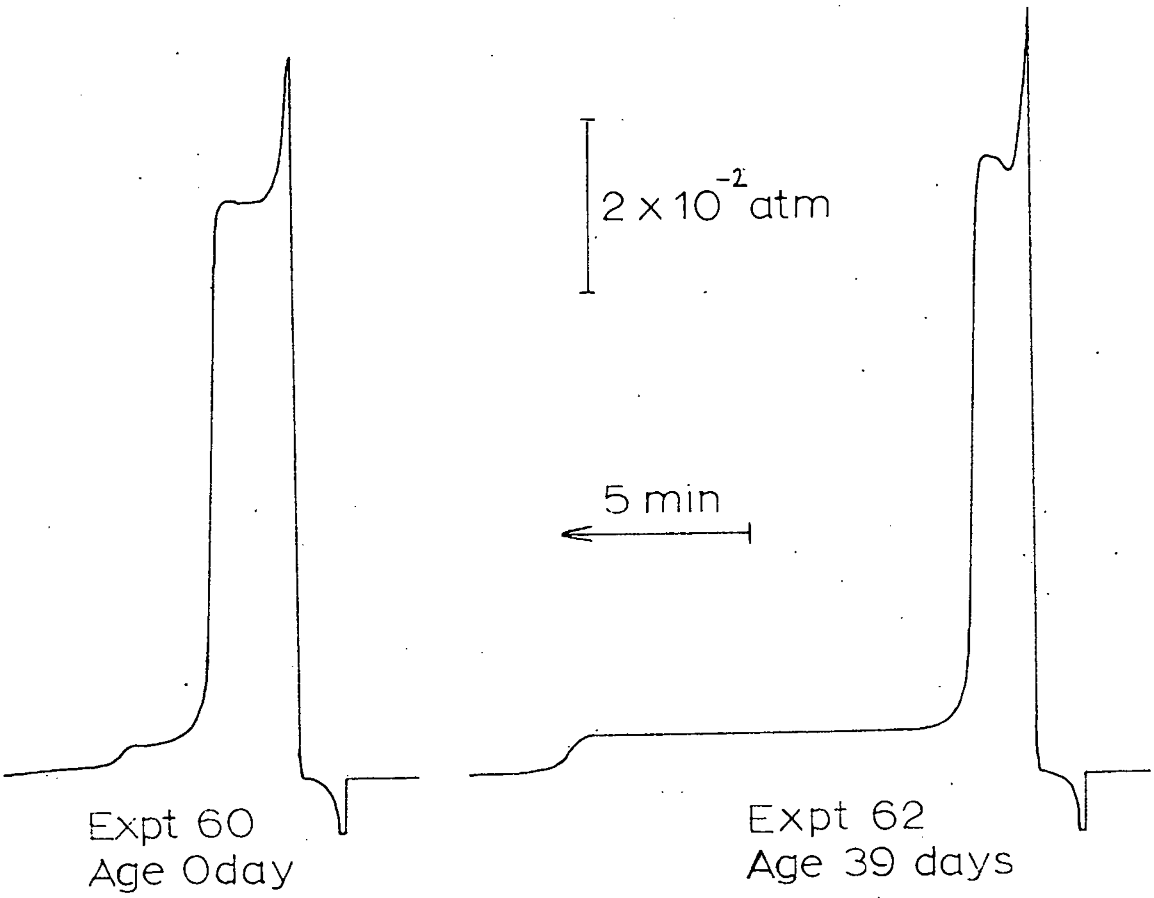

Figure 18. Silver nitrate in benzyl cyanide — effect of packing age. Packing NBC6, column length 91.3 cm, sample 33(5)-33(9) μmole, flow-rate 34.4-34.5 cm^{3}min^{-1}, column temp. 17.2-18.5°C.

(a) Numerical results

In Table 5 are listed value of P_d (called P_8 according to the classification proposed in 5.1, p.129), V_c and y for the lower plateau; the last column shows the age of the packings for comparison with ages in Tables 8-10.

Table 5 Silver nitrate in benzyl cyanide - experimental conditions and results for the lower plateau

Expt. no.	Flow-rate $cm^3\ min^{-1}$	Sample µmole	Column temp. deg C	$10^3\ P_8$ atm	$10^{-6}\ V_c$ $cm^3\ mole^{-1}$	y	Age days
Packing NBC1, 90.0 cm, 38 µmole silver nitrate, 0.42 µmole cm^{-1}							
1	34.5	45	18.3	4.9(7)	4.2(0)	0.87	5
2	34.3	112	17.7	4.9(7)	4.9(4)	1.03	5
3	34.2	179	17.9	5.1(1)	5.0(6)	1.08	5
Packing NBC1, 171.0 cm, 72 µmole silver nitrate, 0.42 µmole cm^{-1}							
4	34.6	112	19.6	5.6(2)	3.8(8)	0.91	4
5	34.7	179	19.0	5.4(2)	4.1(0)	0.93	4
Packing NBC1, 254.0 cm, 106 µmole silver nitrate, 0.42 µmole cm^{-1}							
6	34.8	45	19.8	-	-	-	3
7	34.8	67	19.8	-	-	-	3
8	34.3	76	19.2	4.5(3)	3.5(5)	0.67	3
9	34.8	82	19.6	4.6(9)	3.6(6)	0.71	3
10	34.3	89	17.9	4.0(8)	4.2(6)	0.73	1
11	34.5	89	17.7	4.2(4)	4.0(9)	0.73	1
12	34.6	89	17.4	4.2(6)	4.0(6)	0.73	1
13	34.8	112	19.7	5.3(1)	3.9(0)	0.86	3
14	34.8	134	19.3	5.3(1)	4.0(2)	0.89	4
15	34.8	156	19.8	6.0(5)	3.8(1)	0.96	4
16	34.8	179	19.8	5.9(1)	3.7(6)	0.92	4
Packing NBC2, 90.0 cm, 72 µmole silver nitrate, 0.80 µmole cm^{-1}							
17	34.2	112	19.7	6.2(9)	3.8(0)	0.99	4
18	34.4	179	21.2	6.5(8)	3.7(6)	1.02	4
Packing NBC2, 171.0 cm, 134 µmole silver nitrate, 0.78 µmole cm^{-1}							
19	34.8	112	20.7	5.5(1)	3.2(7)	0.75	2
20	34.2	179	20.0	5.7(3)	3.5(3)	0.84	2
Packing NBC2, 254.0 cm, 201 µmole silver nitrate, 0.79 µmole cm^{-1}							
21	34.6	89	19.5	3.7(9)	2.7(2)	0.43	1
22	34.6	112	18.2	3.9(5)	3.1(8)	0.53	1
23	33.8	122	20.0	4.6(4)	2.9(6)	0.57	1
24	34.4	134	19.6	4.4(6)	3.1(8)	0.59	0
25	34.3	134	19.0	4.6(4)	3.3(2)	0.64	0
26	34.5	134	18.4	4.2(2)	3.3(0)	0.58	0
27	34.8	156	20.1	5.0(2)	3.3(8)	0.71	2
28	34.1	179	19.3	4.6(8)	3.6(8)	0.72	1

Table 5 (continued)

Expt. no.	Flow-rate $cm^3 min^{-1}$	Sample µmole	Column temp. deg C	10^3 P_6 atm	10^{-6} V_C $cm^3 mole^{-1}$	y	Age days
Packing NBC3;* 94.9 cm, 93 µmole silver nitrate, 0.98 µmole cm^{-1}							
29	34.3	112	18.8	5.0(9)	2.9(0)	0.62	7
30	34.9	112	17.7	4.8(9)	3.1(1)	0.64	9
31	29.6	112	18.0	5.0(9)	3.0(2)	0.64	9
32	24.0	111	18.2	5.1(3)	3.0(5)	0.66	9
33	18.8	112	18.7	5.0(9)	3.0(6)	0.65	9
34	13.5(7)	111	18.7	5.3(6)	3.2(0)	0.72	9
35	7.2(4)	112	18.1	5.3(6)	3.1(4)	0.70	9
Packing NBC3;* 175.9 cm, 173 µmole silver nitrate, 0.98 µmole cm^{-1}							
36	34.9	112	18.0	4.3(5)	2.6(4)	0.48	7
37	34.8	155	18.0	4.7(5)	2.8(2)	0.56	7
38	35.3	155	18.4	5.0(6)	2.6(6)	0.56	10
39	19.4	156	18.7	5.3(1)	2.8(0)	0.62	10
Packing NBC3;* 257.9 cm, 253 µmole silver nitrate, 0.99 µmole cm^{-1}							
40	34.9	155	17.0	3.8(6)	3.0(1)	0.49	7
41	34.3	237	17.5	4.6(4)	3.1(0)	0.60	7
Packing NBC4, 90.0 cm, 105 µmole silver nitrate, 1.17 µmole cm^{-1}							
42	34.2	54	20.4	4.4(6)	2.7(3)	0.51	12
43	34.4	68	20.1	4.6(8)	3.3(0)	0.64	12
44	34.4	89	19.3	4.4(6)	4.2(7)	0.79	12
45	34.1	112	20.3	5.2(9)	4.3(3)	0.95	11
46	34.5	179	19.0	5.2(0)	4.5(8)	0.99	11
47	7.8(4)	68	20.6	4.6(8)	3.2(9)	0.64	12
Packing NBC4, 171.0 cm, 198 µmole silver nitrate, 1.16 µmole cm^{-1}							
48	34.2	101	20.1	4.3(9)	2.9(0)	0.53	10
49	34.1	112	20.2	4.6(2)	3.0(5)	0.59	10
50	34.5	179	18.2	4.3(3)	4.2(5)	0.77	10
51	16.2	94	20.5	4.5(9)	2.7(1)	0.52	14
Packing NBC4, 254.0 cm, 293 µmole silver nitrate, 1.15 µmole cm^{-1}							
52	34.3	112	17.7	3.2(8)	2.8(9)	0.40	9
53	34.2	141	20.2	4.1(9)	2.7(5)	0.48	9
54	34.3	154	19.3	4.1(5)	2.9(8)	0.52	9
55	34.0	167	18.6	3.9(5)	3.1(9)	0.53	8
56	34.5	171	19.2	4.2(4)	3.3(0)	0.58	8
57	34.3	179	18.8	4.1(7)	3.2(8)	0.57	7
58	34.8	224	18.8	4.3(7)	3.5(3)	0.64	7

* Experiments with Packing NBC3 were made with an uncalibrated katharometer exactly similar to the calibrated one. The calibration factor determined for the latter is assumed to be valid for the other.

The following trends are noticeable :

(i) P_6 increases with increase in sample size;

(ii) V_c and y increase with decrease in column length;

(iii) V_c and y increase with decrease in silver nitrate concentration;

(iv) V_c and y increase with increase in sample size.

(i) and (ii) are possibly due to decay of zone II (see 2.3.1, p. 13) as it passes through the column, this decay resulting from the peak-broadening (and peak-flattening) factors mentioned in 2.2.1, p. 11 . (iii) is discussed in 4.4.6, p. 59 . (iv) may be the effect shown to a much more marked degree by silver perchlorate in fenchone and ascribed to incomplete conversion of the salt in zone I to ammine, the degree of conversion increasing with increase in the ammonia pressure in zone I (see 4.9.4, p. 84); this cause may also contribute to (ii), since the ammonia pressure in zone I falls with increasing distance from the column inlet.

The stoichiometric significance of the values of y recorded in Table 5 is discussed in 4.4.7, p. 60 .

The average and standard deviation of the values of P_e recorded in Tables 5 and 9 (p. 60), obtained at 17.0 to 21.2°C, are 4.66×10^{-3} atm and 0.66×10^{-3} atm.

(b) <u>Comparison of Methods 1 and 2</u>

In the experiments listed in Table 6, the complete chromatogram, including the whole tail, was recorded. The high and variable values of C and the discrepancies between columns 2 and 4 show that the effective sample size is less than the measured size (see 2.6, p. 22). There is fair agreement between Methods 1 and 2 if the effective sample size is used in Method 1. The average value of t_e/t_h is 1.13 and provides a good approximation of t_e for use in Method 2, as shown by a comparison of columns 7 and 8.

Table 6 Silver nitrate in benzyl cyanide - comparison of Methods 1 and 2

Expt. No.	10^3 C atm cm^{-1}	y by Method 1			t_e/t_h	y by Method 2	
		Measured sample	Effective sample	Pub-lished		Ideal plateau	Approxi-mation
8	3.0(5)	1.09	0.78	0.74	1.13	0.68	0.67
9	2.9(8)	1.14	0.85	0.77	1.16	0.74	0.71
23	2.7(6)	0.82	0.65	0.53	1.18	0.60	0.57
40	3.1(6)	0.80	0.56	0.53	1.10	0.48	0.49
47	2.7(4)	0.87	0.63	0.60	1.12	0.63	0.64
48	2.9(5)	0.73	0.54	0.48	1.09	0.51	0.53
51	3.0(2)	0.75	0.54	0.51	1.18	0.54	0.52
53	2.8(1)	0.68	0.54	0.43	1.14	0.49	0.48
54	2.8(5)	0.72	0.55	0.45	1.08	0.50	0.52
55	2.8(9)	0.73	0.56	0.45	1.07	0.50	0.53

In column 5 are listed values of y that were published[30] before the refinements of Method 1 described in 2.5.3, p.21 , and 2.6, p.22, had been devised. The measured sample size was used in calculating these values, while the end of the plateau and the plateau area were chosen as described in the last paragraph of 2.5.3, p.21. The errors introduced by these two faulty procedures tend to cancel and produce some agreement between columns 4 and 5. However, this agreement is fortuitous, since the discrepancy between the measured and effective sample sizes depends on the time of sweeping between experiments, whereas the error arising from incorrect choice of the rear end of the plateau does not.

4.4.4 The dissociation pressure of the ammine responsible for initial absorption

Table 7 shows values of P_d (called P_7) for the ammine responsible for initial absorption, calculated by the method of 2.6, p.22 .

Table 7 Silver nitrate in benzyl cyanide-dissociation pressure of ammine responsible for initial absorption

Expt. no. (m + 1)	V_t $cm^3\ min^{-1}$	t_m min	10^3 P_7 atm
8	34.3	92	0.15
23	33.8	132	0.13
48	34.2	130	0.14
53	34.2	180	0.11
54	34.3	190	0.13
55	34.0	240	0.12

The approximate constancy of P_7 over the range of t_m provides support for the view that a portion of each sample is absorbed in replenishment of ammonia lost by the ammine whose formation causes the initial absorption. The values of P_7 were obtained at 18.6 to 20.2° C, and have an average and standard deviation of 0.13×10^{-3} atm and 0.01×10^{-3} atm.

4.4.5 The higher plateau

Chromatograms obtained with concentrated solutions and larger samples show two plateaux (Fig. 18) and some valley formation (see 2.3.2, p.15) in the higher plateau. The characteristics of the latter are recorded in Table 8, P_d being called P_1. Since the plateau has a steep rear boundary, t_h is probably a good approximation for t_e and is used in the calculation of V_o.

y is discussed in 4.4.6 and 4.4.7. The values of P_1, obtained at 17.2 to 18.5°C, have an average and standard deviation of 67.6×10^{-3} atm and 3.5×10^{-3} atm.

Table 8 Silver nitrate in benzyl cyanide-experimental conditions and results for the higher plateau

Expt. no.	Flow-rate $cm^3\ min^{-1}$	Sample μmole	Column temp. deg C	$10^3\ P_1$ atm	$10^{-5}\ V_c$ $cm^3\ mole^{-1}$	y	Age days
Packing NBC6, 91.3 cm, 564 μmole silver nitrate, 6.18 μmole cm^{-1}							
59	33.9	33(9)	17.3	67.(7)	1.7(6)	0.50	0
60	34.5	33(9)	17.2	68.(4)	1.7(7)	0.51	0
61	34.2	33(5)	18.2	71.(3)	1.4(5)	0.43	39
62	34.4	33(5)	18.5	72.(5)	1.4(4)	0.44	39
Packing NBC7, 92.2 cm, 566 μmole silver nitrate, 6.13 μmole cm^{-1}							
70	34.5	33(8)	17.2	63.(3)	1.2(9)	0.34	33
71	34.3	33(8)	17.3	63.(6)	1.4(1)	0.38	33
Packing NBC8, 90.9 cm, 566 μmole silver nitrate, 6.23 μmole cm^{-1}							
72	34.3	33(7)	17.8	66.(6)	1.7(3)	0.48	0
73	34.3	33(7)	17.8	67.(2)	1.7(5)	0.49	0

4.4.6 Changes on ageing

Table 9 presents some data on the lower plateau for immature packings, V_c being calculated by using the value 1.13 for t_e/t_h. Although these data are fragmentary, they clearly show two properties of the lower plateau : y has small fractional values for an immature packing and increases with lapse of time. From Table 8 it is evident that y for the higher plateau decreases with lapse of time. In Table 10 are listed experiments giving values of y for both plateaux (y_L for lower plateau, y_H for higher). The quantities y_H/y_L and $y_H + y_L$ are listed for discussion in 4.4.7.

The increase of y_L with age and the higher rate of this increase for lower silver nitrate concentrations are a possible explanation of the trend (iii) of 4.4.3 (a), viz increase of V_c and y_L with decrease in silver nitrate concentration.

No packing was tested over a long enough period to ensure that the ageing process was completed, and it is therefore not known whether Packings NBC1, NBC2, NBC3 and NBC4 were mature when used.

Table 9 Silver nitrate in benzyl cyanide - the lower plateau with immature packings

Expt. no.	Flow-rate cm^3 min^{-1}	Sample μmole	Column temp. deg C	10^3 P_G atm	10^{-5} V_G cm^3 $mole^{-1}$	y	Age days
Packing NBC6, 91.3 cm, 564 μmole silver nitrate, 6.18 μmole cm^{-1}							
59	33.9	33(9)	17.3	4.0(2)	3.6(2)	0.061	0
60	34.5	33(9)	17.2	4.3(7)	3.7(0)	0.068	0
61	34.2	33(5)	18.2	4.6(4)	8.0(2)	0.156	39
62	34.4	33(5)	18.5	4.7(7)	8.3(9)	0.167	39
Packing NBC7, 92.2 cm, 566 μmole silver nitrate, 6.13 μmole cm^{-1}							
63	34.6	143	17.3	4.1(7)	3.0(2)	0.053	0
64	34.6	143	17.3	4.2(2)	3.1(6)	0.056	0
65	34.3	143	17.1	3.6(4)	3.6(4)	0.056	8
66	34.3	143	17.5	3.7(9)	3.7(0)	0.059	8
67	34.5	144	17.3	3.7(5)	6.9(3)	0.109	24
68	34.5	144	17.3	3.8(6)	7.5(5)	0.122	24
69	34.7	144	17.0	3.6(1)	8.5(1)	0.129	33
70	34.5	33(8)	17.2	3.8(4)	11.2(9)	0.182	33
71	34.3	33(8)	17.3	3.8(8)	11.8(0)	0.192	33
Packing NBC8, 90.9 cm, 566 μmole silver nitrate, 6.23 μmole cm^{-1}							
72	34.3	33(7)	17.8	4.4(6)	5.9(0)	0.110	0
73	34.3	33(7)	17.8	4.5(1)	5.9(5)	0.112	0

Table 10 Silver nitrate in benzyl cyanide - comparison of plateaux

Expt. no.	Packing	Age days	y_L	y_H	y_H/y_L	$y_H + y_L$
59	NBC6	0	0.061	0.50	8.2	0.56
60	"	0	0.068	0.51	7.5	0.58
61	"	39	0.156	0.43	2.8	0.59
62	"	39	0.167	0.44	2.6	0.61
70	NBC7	33	0.182	0.34	1.9	0.52
71	"	33	0.192	0.38	2.0	0.57
72	NBC8	0	0.110	0.48	4.4	0.59
73	"	0	0.112	0.49	4.4	0.60

4.4.7 Stoichiometric interpretation

In the absence of quantitative data on y_L and y_H, the obvious interpretation of the initial absorption and chromatograms like those shown in Fig. 18 would be that all or some of the silver nitrate in the column reacted as follows :

$$AgNO_3 + xNH_3 \rightleftharpoons AgNO_3(NH_3)_x, \qquad p_{NH_3} = P_7$$

$$AgNO_3(NH_3)_x + yNH_3 \rightleftharpoons AgNO_3(NH_3)_{x+y}, \qquad p_{NH_3} = P_6 \quad \ldots\ldots\ldots \quad (i)$$

$$AgNO_3(NH_3)_{x+y} + zNH_3 \rightleftharpoons AgNO_3(NH_3)_{x+y+z}, \quad p_{NH_3} = P_1 \quad \ldots\ldots\ldots \quad (ii)$$

x, y, z being integers or simple fractions.

That this interpretation is incorrect is shown by the inconstancy of y_H/y_L (see Table 10); for equations (i) and (ii) require this ratio to be constant. Thus different portions (and different forms) of the silver salt must be responsible for the two plateaux :

$$AgW + wNH_3 \rightleftharpoons AgW(NH_3)_w, \qquad p_{NH_3} = P_6 \quad \ldots\ldots\ldots(iii)$$

$$AgZ + zNH_3 \rightleftharpoons AgZ(NH_3)_z, \qquad p_{NH_3} = P_1 \quad \ldots\ldots\ldots \quad (iv)$$

Either AgW or AgZ, or both, may contain some or all of the initially absorbed ammonia, as well as benzyl cyanide (see 5.1, p.129). AgZ changes into AgW with passage of time.

The higher values of y in Table 5 suggest the value of 1 for w in equation (iii). The comparatively low values of $y_H + y_L$ in Table 10 may perhaps mean that some of the silver salt is present in a form other than AgW or AgZ, that forms no plateau observable under the experimental conditions used. If this is not the case, the value 0.5 is indicated for z in equation (iv).

Some support for the view that the silver salt exists in different forms in the column is provided by the results of attempts to extract the silver from Packing NBC5 after the initial absorption of ammonia had taken place. A portion of the packing was agitated with the extracting liquid, which was then decanted and titrated with standard potassium thiocyanate solution; extraction was repeated till the extract contained no silver. Dilute nitric acid (15%) removed all the silver from the packing, leaving it white, but extraction of three portions with water removed only 58%, 58% and 54% of the silver, leaving the packing grey. These results may mean that the silver salt is present in different forms, of which not all are soluble in water. It is, however, also possible that some of the salt is decomposed by the extracting water, for the percentage of silver extractable by water (average 57%) is not related to the initial absorption by Packing NBC5 (1.4 mole ammonia per mole of salt) in a way that permits a simple stoichiometric interpretation.

4.5 Silver perchlorate in benzyl cyanide

Packings containing silver perchlorate in benzyl cyanide have not been exhaustively studied, but enough results have been obtained to establish the following properties of such packings :

(i) initial absorption of ammonia takes place;

(ii) at least three plateaux are present in the chromatograms;

(iii) the chromatograms are influenced both by the age of the packing and by the age of the solution used to prepare the packing.

A white precipitate is formed on treating a solution of silver perchlorate in benzyl cyanide with ammonia, so that such a solution acts as a heterogeneous fixed phase.

4.5.1 The packings

Table 11 shows the characteristics of the packings; in column 4 is given the age of the solution when it was mixed with the glass beads. Packings PBC1, PBC2 and PBC3 turned pale mauve soon after preparation and before injection of ammonia, but showed no further colour change, while Packing PBC4 remained almost white.

4.5.2 The initial absorption

Packing PBC4 showed an initial absorption of 1.4 mole of ammonia per mole of silver perchlorate.

Table 11 Packings containing silver perchlorate in benzyl cyanide

Packing	Concentration µmole cm^{-3}	10^2 s cm^3 g^{-1}	Age of solution days	Benzyl cyanide redistilled
PBC1	64.7	3.00	0	No
PBC2*	138.3	3.00	6	Yes
PBC3*	138.3	3.00	13	Yes
PBC4*	138.3	3.00	69	Yes

* Packings PBC2, PBC3 and PBC4 were prepared from the same solution.

4.5.3 The chromatograms

The chromatograms in Figs. 19 and 20 show the three plateaux observed and the effect of solution age and packing age. The plateaux are marked I, II and III in order of decreasing height and have pressures P_2, P_5 and P_6 respectively.

4.5.4 Numerical results

The results in Table 12 are listed in chronological order for each packing. t_e/t_h is assumed to be 1 for plateau I; for the other plateaux, the averages found in 4.5.5 are used.

Table 12 Silver perchlorate in benzyl cyanide - experimental conditions and results

Expt. no.	Flow-rate cm^3 min^{-1}	Sample µmole	Column temp. deg C	10^3 P_d atm		10^{-6} V_c cm^3 $mole^{-1}$		y		Age days
				P_5	P_6	Plat II	Plat III	Plat II	Plat III	
Packing PBC1, 90.3 cm, 92µmole silver perchlorate, 1.02 µmole cm^{-1}										
1	31.9	202	22.4	8.3(8)	-	3.2(5)	-	1.12	-	1
2	34.2	120	20.8	7.3(6)	-	3.2(4)	-	0.99	-	31
3	34.0	99	22.7	7.8(1)	-	3.0(5)	-	0.98	-	31
4	34.0	78	23.1	7.8(1)	-	2.9(9)	-	0.96	-	31
5	34.0	58	23.0	7.1(4)	-	2.5(2)		0.74	-	31
Packing PBC2, 90.0 cm, 194 µmole silver perchlorate, 2.16 µmole cm^{-1}										
6	9.6(8)	32(2)	23.7	8.3(5)	-	2.6(6)	-	0.91	-	3
7	9.7(3)	200	23.7	9.0(5)	-	2.3(8)	-	0.88	-	3
8	9.6(8)	160	22.1	7.9(4)	-	2.4(8)	-	0.81	-	4
9	32.4	159	22.1	8.2(3)	-	2.4(9)	-	0.85	-	6
10	32.5	142	20.7	6.7(6)	-	2.4(8)	-	0.69	-	6
11	32.5	133	21.5	7.3(6)	-	2.2(3)	-	0.68	-	7

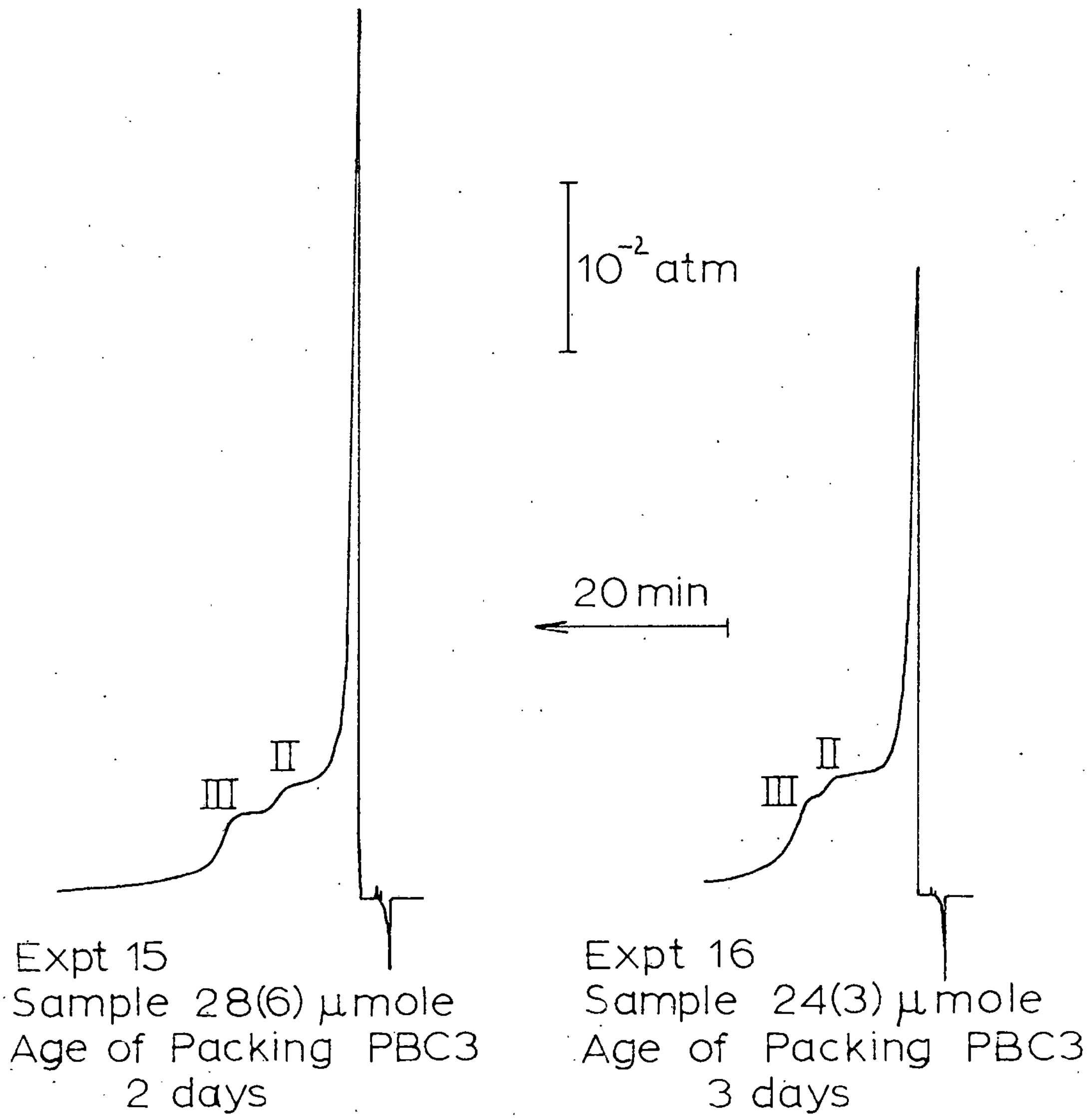

Figure 19. Silver perchlorate in benzyl cyanide. Packing PBC2 followed by Packing PBC3, column length 171.0 cm, flow-rate 35.1-36.6 $cm^3 min^{-1}$, column temp. 20.8-22.0°C.

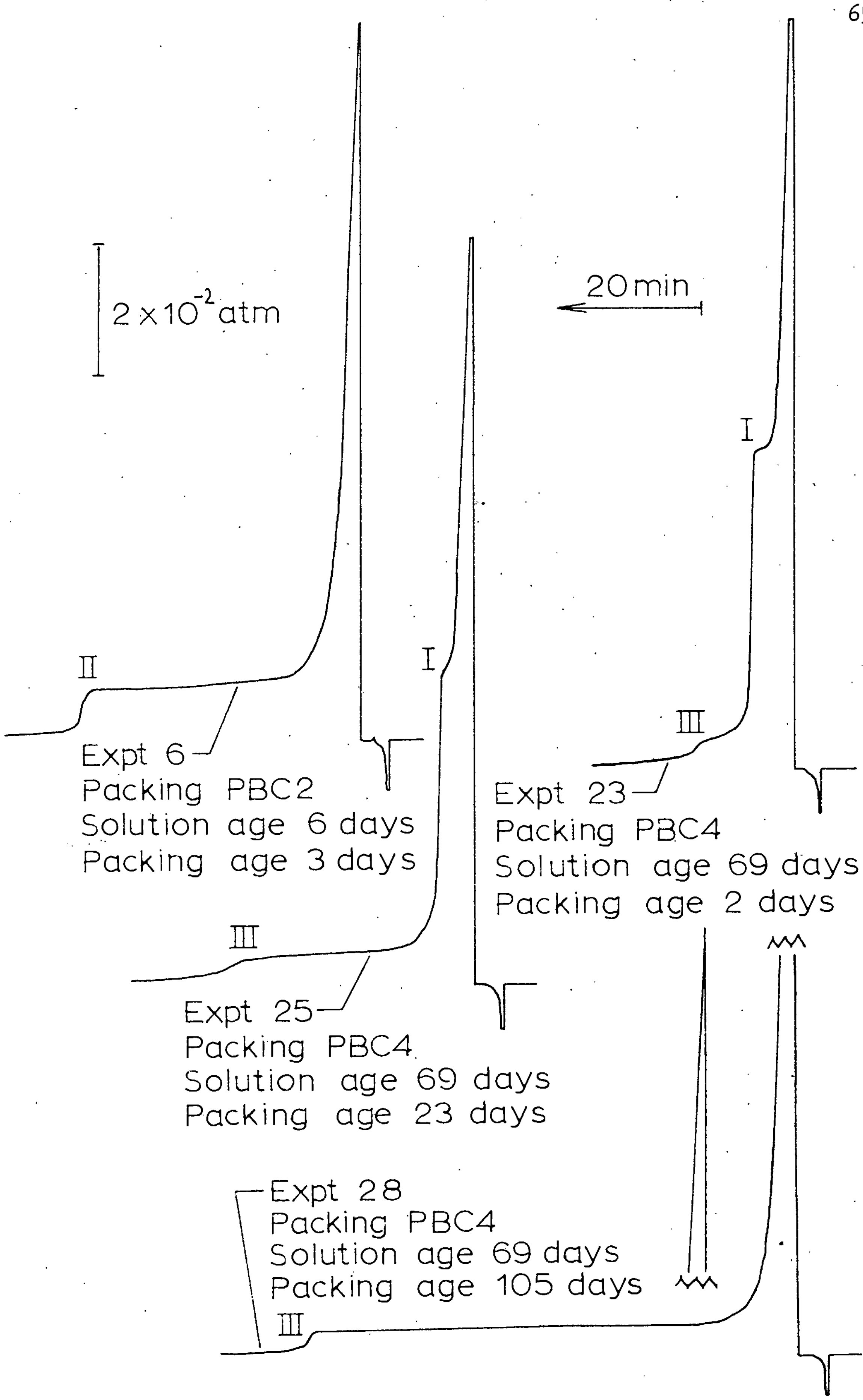

Figure 20. Silver perchlorate in benzyl cyanide —effect of solution age and packing age. Column length 90.0 cm (PBC2) and 81.9 cm (PBC4), flow-rate 9.6(8)-9.8(9) $cm^3\,min^{-1}$, sample 32(2)-33(9) μmole, column temp. 17.1-23.7°C.

Table 12 (continued)

Expt. no.	Flow-rate cm^3 min^{-1}	Sample µmole	Column temp. deg C	10^3 P_d atm		10^{-6} V_c $cm^3 mole^{-1}$		y		Age days
				P_5	P_6	Plat II	Plat III	Plat II	Plat III	
12	33.1	112	19.7	-	5.3(1)	-	2.6(3)	-	0.58	41
90.0 cm Packing PBC2, followed by 81.0 cm Packing PBC3; 352 µmole silver perchlorate										
13	35.7	41(0)	21.7	7.8(1)	6.6(7)	1.0(9)	1.8(9)	0.35	0.52	0*
14	36.6	28(7)	20.3	7.2(0)	5.3(6)	1.2(4)	1.9(9)	0.37	0.44	1*
15	36.6	28(6)	20.8	7.0(3)	5.1(3)	1.2(4)	1.9(2)	0.36	0.41	2*
16	35.1	24(3)	22.0	7.2(3)	5.8(9)	1.3(4)	1.7(1)	0.40	0.42	3*
17	33.7	32(7)	21.8	6.8(7)	5.3(1)	1.6(5)	1.8(7)	0.47	0.41	9*
18	34.9	205	18.2	-	4.0(8)	-	2.6(0)	-	0.45	30*
19	34.2	21(8)	18.9	-	4.7(5)	-	2.4(5)	-	0.49	31*
20	34.2	23(0)	18.8	-	4.9(3)	-	2.4(8)	-	0.51	32*
21	34.1	22(4)	19.0	-	4.9(9)	-	2.3(5)	-	0.49	32*
				P_2	P_6	Plat I	Plat III	Plat I	Plat III	
Packing PBC4, 81.9 cm, 194 µmole silver perchlorate, 2.37 µmole cm^{-1}										
22	34.4	82(4)	18.4	49.(2)	5.0(2)	0.47	1.0(6)	0.9(7)	0.22	2
23	9.6(9)	32(7)	18.2	50.(4)	5.0(4)	0.42	0.9(5)	0.8(9)	0.20	2
24	9.7(9)	24(4)	18.6	51.(5)	4.9(5)	0.46	0.9(0)	0.9(9)	0.19	2
25	9.8(9)	32(8)	18.0	49.(1)+	5.1(3)	0.40	2.2(5)	0.8(2)	0.48	23
26	9.7(5)	33(3)	17.3	46.(4)+	4.4(6)	0.40	2.6(1)	0.7(8)	0.49	30
27	9.8(5)	33(6)	17.5	-	5.2(6)	-	3.4(2)	-	0.75	60
28	9.7(0)	33(9)	17.1	-	4.0(2)	-	4.2(7)	-	0.72	105
29	33.6	127	17.3	-	4.5(3)	-	3.2(2)	-	0.61	105
30	33.6	106	17.3	-	4.3(7)	-	3.0(8)	-	0.56	105

* Age of Packing PBC3.

\+ Plateau vestigial, P_2 not used in calculation of average.

It appears that plateaux II and III in Expts. 13-17 are due to Packings PBC2 and PBC3 respectively, for Expts. 11 (PBC2 alone) and 13 (PBC2 + PBC3) were made on the same day, and plateau III did not appear in Expt. 11. Therefore V_c and y for Expts. 13-17 do not have their usual significance and are given for comparison only.

The temperature ranges within which P_2, P_5 and P_6 were determined and the averages and standard deviations of these pressures are as follows :

P_2 18.2 - 18.6°C, 50.4 x 10^{-3} atm, 1.2 x 10^{-3} atm

P_5 20.3 - 23.7°C, 7.65 x 10^{-3} atm, 0.64 x 10^{-3} atm

P_6 17.1 - 22.0°C, 5.01 x 10^{-3} atm, 0.60 x 10^{-3} atm

4.5.5 Comparison of Methods 1 and 2

Table 13 shows values of y for plateaux II and III, calculated by different methods.

Table 13 Silver perchlorate in benzyl cyanide - comparison of Methods 1 and 2

Expt. no.	Plateau	10^3 C atm cm^{-1}	y by Method 1		t_e/t_h	y by Method 2	
			Measured sample	Effective sample		Ideal plateau	Approxi-mation
10	II	2.9(7)	0.95	0.71	1.26	0.68	0.69
11	"	2.9(2)	1.01	0.77	1.35	0.70	0.68
12	III	2.7(6)	0.75	0.59	1.17	0.55	0.58
18	"	3.6(3)	0.77	0.47	1.17	0.42	0.45
19	"	3.1(2)	0.83	0.58	1.33	0.53	0.49
20	"	2.5(3)	0.76	0.64	1.41	0.60	0.51
21	"	2.7(4)	0.74	0.60	1.33	0.54	0.49
29	"	2.2(9)	0.64	0.57	1.08	0.54	0.61
30	"	2.3(6)	0.59	0.55	1.14	0.52	0.56

The high and variable values of C and the discrepancies between columns 3 and 5 indicate impermanence of the initial absorption (see 2.6, p.22) and the agreement between Methods 1 and 2 is much improved by using the effective sample size in Method 1. The average values of t_e/t_h for plateaux II and III are 1.31 and 1.23 respectively.

4.5.6 The dissociation pressure of the ammine responsible for initial absorption

Application of the method described in 2.6, p.22 , gives the values in Table 14 for the dissociation pressure (P_7) of the ammine responsible for initial absorption. P_7 was determined at 18.8 to 21.5°C and has an average and standard deviation of 0.14 x 10^{-3} atm and 0.03 x 10^{-3} atm.

Table 14 Silver perchlorate in benzyl cyanide - dissociation pressure of ammine responsible for initial absorption

Expt. no. (m+1)	V_t cm^3 min^{-1}	t_m min	10^3 P_7 atm
11	32.5	180	0.13
19	34.2	380	0.12
20	34.2	200	0.13
21	34.1	163	0.18

4.5.7 Changes on ageing

The existence of prolonged and complicated ageing effects was not suspected when the study of silver perchlorate in benzyl cyanide was started, and the data on these effects are therefore unsystematic and very incomplete. When not in use, the columns were stoppered and stored in a dark cupboard, so the ageing took place at room temperature.

The lean packing, PBC1, shows no replacement of one plateau by another up to an age of 31 days (Expts. 1-5). In the chromatograms obtained with Packing PBC2, only plateau II is present at ages of 3 to 7 days (Expts. 6-11), but at 41 days has been replaced by plateau III (Expt. 12). There is no record of plateau I for Expts. 1-5 and 9-21, because with the unattenuated bridge output used, this plateau is off the recorder scale. Packing PBC4 shows plateaux I and III initially, but plateau III gradually lengthens while plateau I shrinks and finally disappears (Expts. 22-30 and Fig. 20).

Not only a used packing, but also an unused solution changes on ageing. Packings PBC2 and PBC3 were prepared from the same solution at ages of 6 and 13 days respectively; in Expt. 11, Packing PBC2 shows only plateau II, whereas on the same day, Packing PBC3 shows plateau III in Expt. 13. Expts. 6 and 23 (see Fig. 20) were made with packings having the similar ages of

3 and 2 days, but prepared from the same solution at the widely differing ages of 6 and 69 days; in Expt. 6 only plateau II is present, while in Expt. 23 only I and III are present.

The foregoing results suggest that the solution, whether unused or in a used packing, undergoes changes that first cause replacement of plateau II by plateaux I and III and then growth of III at the expense of I. Expts. 13-17 seem to show an exception to this generalization, since y for plateau II increases and y for plateau III decreases with time. Comparison of the results of these experiments is however hampered by the inconstancy of sample size, a variable which generally has some influence on y.

4.5.8 Stoichiometric interpretation

The simultaneous growth of plateau III and disappearance of plateau I in Expts. 22-28 show that these plateaux are due to two different forms of the silver salt (cf. 4.4.7, p. 60); probably plateau II is due to a third form.

The higher values of y in Table 12 suggest that each of the three ammines responsible for the three plateaux dissociates with the loss of 1 mole of ammonia per mole of silver perchlorate.

4.5.9 The effect of moisture

Since silver perchlorate is deliquescent, it was thought that absorption of moisture might influence the behaviour of a packing. This possibility was investigated for Packing PBC1 after completion of Expts. 1-5; a drop of water was placed on the packing at its upstream end and evaporated by the flowing carrier gas. When all the moisture had been eluted, an ammonia chromatogram still showed plateau II (8.10×10^{-3} atm at 24.4°C), proving that the moisture had passed through without affecting the packing. This indicates that the structural positions normally taken up by water are occupied by the initially absorbed ammonia or by benzyl cyanide (see 5.1, p.129).

4.6 Silver nitrate in benzonitrile

Packings containing silver nitrate in benzonitrile absorb ammonia initially, then give chromatograms with one plateau (P_1) and show no changes on ageing. The results of two tensimetric experiments agree roughly with the gas-chromatographic results.

Silver nitrate in benzonitrile reacts with ammonia to form a white precipitate and therefore acts as a heterogeneous fixed phase.

4.6.1 The packings

The packings (Table 15) were prepared from May and Baker silver nitrate and redistilled benzonitrile; they turned dark grey soon after preparation, before ammonia was injected, and showed no further colour change.

Table 15 Packings containing silver nitrate in benzonitrile

Packing	Concentration μmole cm^{-3}	10^2 s cm^3 g^{-1}
NBN1	365	3.00
NBN2	449	3.00

4.6.2 The initial absorption

Packings NBN1 and NBN2 showed initial absorptions of 1.7 and 1.4 mole of ammonia per mole of silver nitrate respectively.

4.6.3 The chromatograms

The chromatograms in Fig. 21 show the effect of sample size and column length, and the presence of slight valley formation (see 2.3.2, p.15).

4.6.4 Numerical results

In Table 16 are listed the experimental conditions and results. The values of V_c and y are probably less accurate than those for the lower plateaux given by solutions in benzyl cyanide,

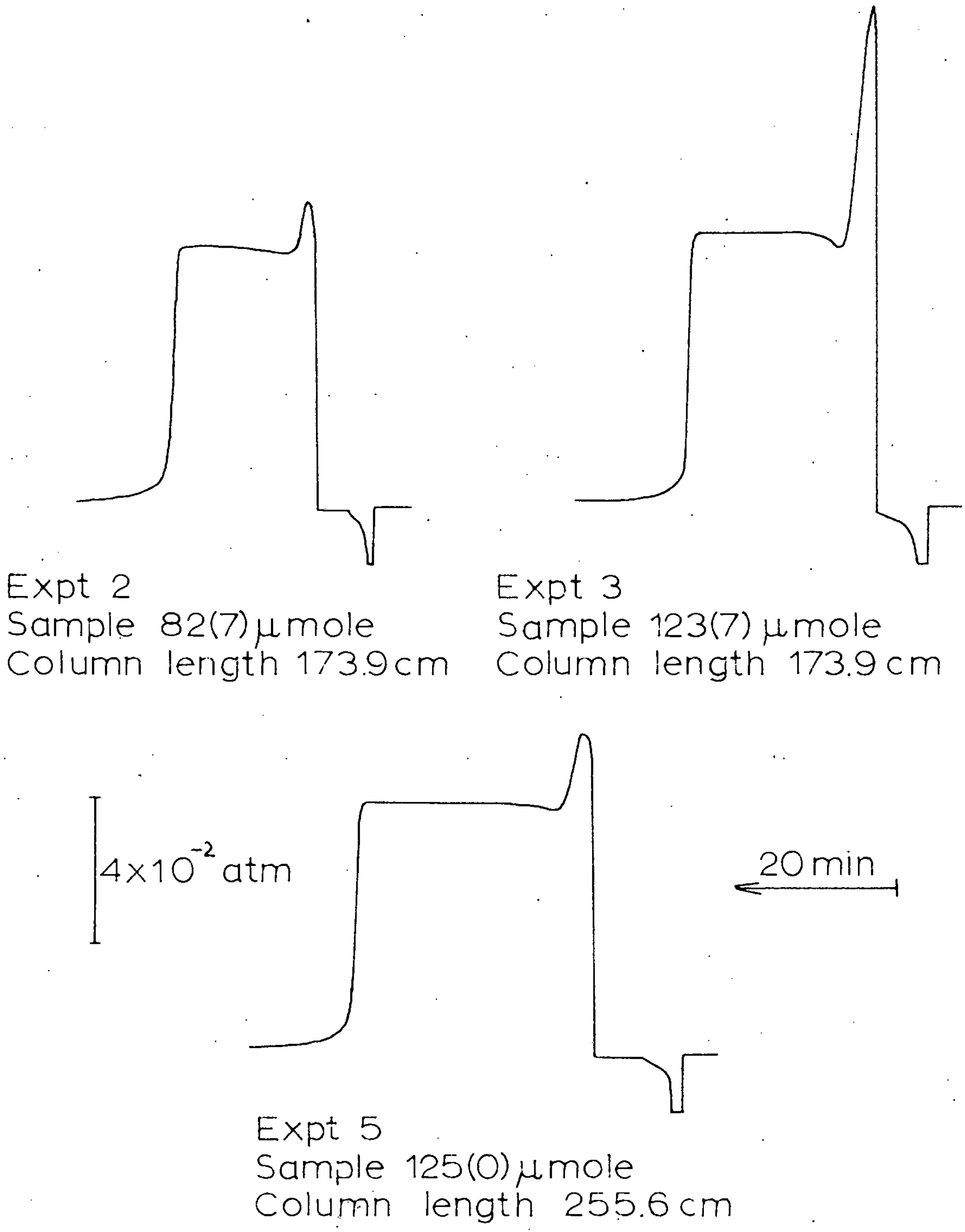

Figure 21. Silver nitrate in benzonitrile — effect of sample size and column length. Packing NBN1, flow-rate 9.9(6)-10.0(6) $cm^3 min^{-1}$, column temp. 16.7-18.2°C.

because the flow-rate used in calculating these quantities is less accurately known for the following reasons :

(i) The measured flow-rate (measured before injection) is that of the carrier gas alone, and is nearly equal to the total flow-rate (which should be used for calculating V_c) only when P_d is low; here P_d is the appreciable fraction 0.07 of the total effluent pressure. The total flow-rate cannot be measured with a soap-film flowmeter, because the ammonia dissolves in the flowmeter liquid.

(ii) The flow-rate varies during an experiment, because a large ammonia sample changes the viscosity of the gas passing through the column appreciably (viscosities at 18°C : N_2, 175 μpoise; NH_3, 106 μpoise). These remarks apply to all high plateaux.

y increases with sample size, and this may be the effect shown to a more marked degree by silver perchlorate in fenchone and ascribed to incomplete conversion of the salt in zone I to ammine, the degree of conversion increasing with increase in the ammonia pressure in zone I (see 4.9.4, p. 84).

P_1 was determined at 16.7 to 19.3°C and has an average and standard deviation of 73.0×10^{-3} atm and 2.0×10^{-3} atm.

Table 16 Silver nitrate in benzonitrile - experimental conditions and results

Expt. no.	Flow-rate $cm^3\ min^{-1}$	Sample μmole	Column temp. deg C	$10^3\ P_1$ atm	$10^{-5}\ V_c$ $cm^3 mole^{-1}$	y
Packing NBN1, 173.9 cm, 947 μmole silver nitrate, 5.45 $\mu mole\ cm^{-1}$						
1	9.7(2)	61(4)	17.9	74.(1)	1.8(6)	0.58
2	10.0(1)	82(7)	17.3	72.(3)	2.3(5)	0.71
3	10.0(6)	123(7)	18.2	76.(5)	2.8(4)	0.91
Packing NBN1, 255.6 cm, 1375 μmole silver nitrate, 5.38 $\mu mole\ cm^{-1}$						
4	9.5(8)	102(7)	18.9	74.(1)	2.0(3)	0.63
5	9.9(6)	125(0)	16.7	69.(8)	2.5(5)	0.75
6	9.7(9)	133(3)	19.3	71.(1)	2.4(9)	0.74
Packing NBN2, 93.0 cm, 638 μmole silver nitrate, 6.86 $\mu mole\ cm^{-1}$						
7	9.8(2)	41(2)	18.1	72.(3)	1.8(8)	0.57
8	9.9(0)	41(3)	18.0	71.(4)	1.8(6)	0.56
9	9.6(4)	83(0)	17.7	74.(1)	2.4(0)	0.74
10	9.7(3)	124(9)	17.3	74.(3)	2.6(0)	0.81

4.6.5 Comparison of Methods 1 and 2

Table 17 shows values of y calculated by different methods. The high and variable values of C and the discrepancies between columns 3 and 4 indicate impermanence of the initial absorption (see 2.6, p.22); good agreement between Methods 1 and 2 results from using the effective sample size in Method 1. t_e/t_h has an average value of 1.05.

Table 17 Silver nitrate in benzonitrile - comparison of Methods 1 and 2

Expt. no.	10^3 C atm cm^{-1}	y by Method 1		t_e/t_h	y by Method 2	
		Measured sample	Effective sample		Ideal plateau	Approximation
1	3.2(0)	0.90	0.60	1.06	0.59	0.58
2	3.2(5)	1.08	0.72	1.03	0.70	0.71
3	3.3(7)	1.40	0.90	1.01	0.87	0.91
4	3.2(9)	0.99	0.64	1.03	0.61	0.63
5	3.0(1)	1.09	0.79	1.04	0.74	0.75
7	3.0(6)	0.83	0.59	1.08	0.59	0.57
8	3.1(5)	0.84	0.58	1.09	0.58	0.56
9	3.6(4)	1.32	0.80	1.08	0.77	0.74

4.6.6 The dissociation pressure of the ammine responsible for initial absorption

The data necessary for calculating the dissociation pressure of the ammine responsible for initial absorption were not recorded, but this pressure must lie below 0.4×10^{-3} atm, the lowest pressure that can be detected by the katharometer (see 4.14.4, p.115).

4.6.7 Tensimetric experiments

Fig. 22 shows the tensimetric curve obtained at 17.5°C for 613 μmole of silver nitrate (Hopkin and Williams) in 0.50 cm^3 of benzonitrile (redistilled), using the apparatus of 3.4, p.37 . The ammonia absorption per mole of silver nitrate is 1.7(9) mole at low pressures ($\not>$ 0.016 atm) and 0.9(7) mole at 0.11(6) atm. From a similar curve for 515 μmole of silver nitrate (Hopkin and Williams) in 0.44 cm^3 of benzonitrile (redistilled) on 13.1 g of glass beads at 17.5°C, the absorption per mole of silver nitrate is 1.4(4) mole at low pressures ($\not>$ 0.011 atm) and 0.7(1) mole at 0.11(1) atm. Both the unsupported and the supported solutions turned dark grey before injection of ammonia.

The following correlation of these results with the gas-chromatographic behaviour of silver nitrate in benzonitrile is suggested: the tensimetric absorption at low pressures (<0.02 atm) corresponds to the initial absorption by a column packing, the absorption at 0.11 - 0.12 atm is due to the formation of the ammine responsible for the chromatogram plateau, and 0.11 - 0.12 atm is the pressure corresponding to the plateau (P_1).

Numerically the tensimetric results agree roughly with the gas-chromatographic results, but are of low accuracy because

(i) even though it took 11 and 3 days to obtain the curves for the unsupported and the supported solutions respectively, enough time was probably not allowed for the attainment of

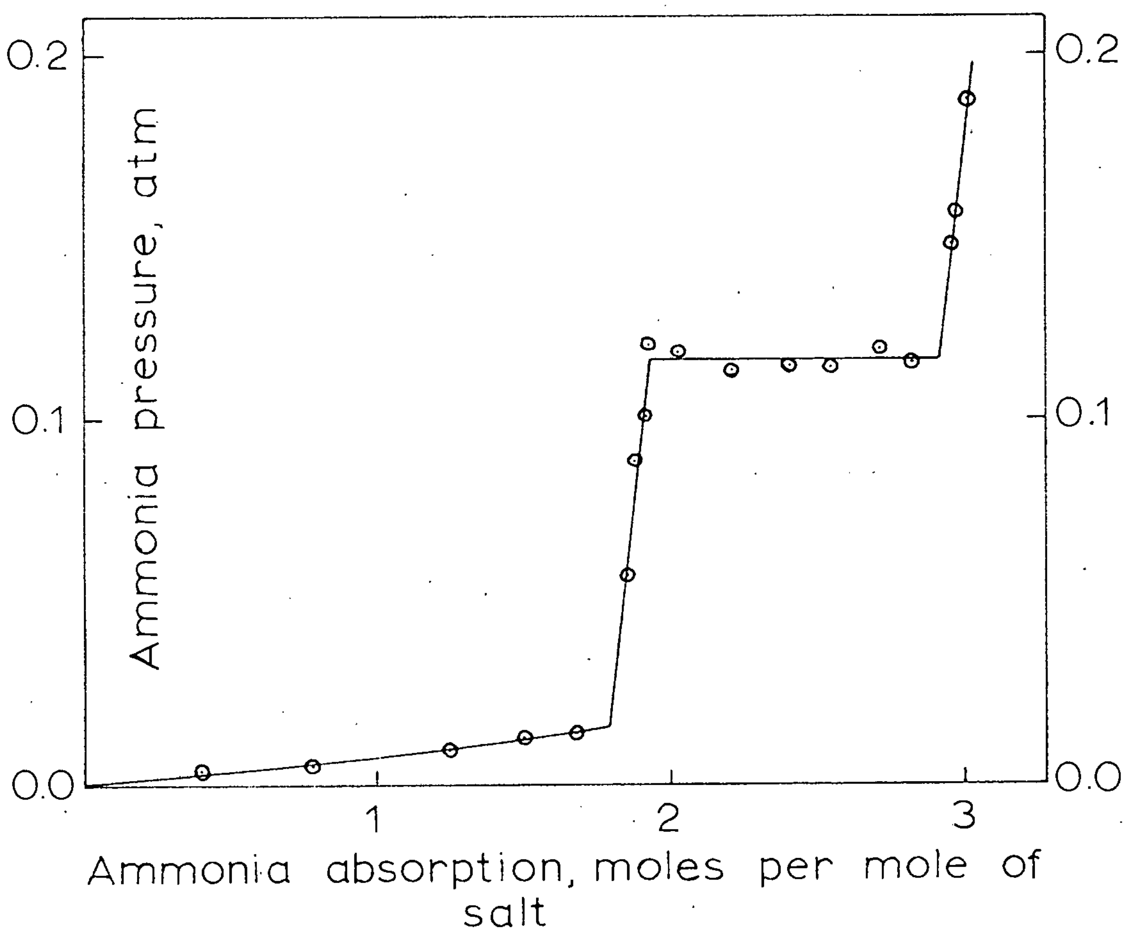

Figure 22. Silver nitrate in benzonitrile —tensimetric curve.

equilibrium - this would explain the initial pressure rise to 0.016 atm and 0.011 atm and the high values of P_1;

(ii) absorption of ammonia by the rubber bung, adsorption on the glass and solution in the benzonitrile are not allowed for; these factors probably explain why the slopes of the steep parts of the tensimetric curves are not infinite.

The long duration of tensimetric experiments renders them unsuitable for investigating systems that change on ageing.

4.6.8 Stoichiometric interpretation

The stoichiometric interpretation of the foregoing results is uncertain because it is not known whether the darkening of the packings is due to decomposition of the silver nitrate and, if so, to what extent such decomposition takes place.

If there is no appreciable decomposition, the values of the initial absorption and the higher values of y in Table 16 indicate the following equations for the column reactions :

$$AgX + 1.5NH_3 \rightleftharpoons AgX(NH_3)_{1.5} \qquad p_{NH_3} < 0.4 \times 10^{-3} atm$$

$$AgX(NH_3)_{1.5} + NH_3 \rightleftharpoons AgX(NH_3)_{2.5} \qquad p_{NH_3} = 73 \times 10^{-3} atm$$

If about 30% of the silver nitrate decomposes to an inert product, the equations may be

$$AgX + 2NH_3 \rightleftharpoons AgX(NH_3)_2 \qquad p_{NH_3} < 0.4 \times 10^{-3} atm$$

$$AgX(NH_3)_2 + 1.5NH_3 \rightleftharpoons AgX(NH_3)_{3.5} \qquad p_{NH_3} = 73 \times 10^{-3} atm$$

4.7 Silver perchlorate in benzonitrile

The chromatography of ammonia on silver perchlorate in benzonitrile closely resembles that on silver nitrate in the same solvent (4.6, p.70), but the plateau is lower.

4.7.1 The packings

The packings were prepared from redistilled benzonitrile and their characteristics are shown in Table 18; they turned dark grey soon after preparation, before ammonia was injected, and showed no further colour change.

Table 18 Packings containing silver perchlorate in benzonitrile

Packing	Concentration µmole cm^{-3}	10^2 s cm^3 g^{-1}
PBN1	138	3.00
PBN2	524	3.00

4.7.2 The initial absorption

Packings PBN1 and PBN2 showed initial absorptions of 1.4 and 1.5 mole of ammonia per mole of silver perchlorate respectively.

4.7.3 The chromatograms

The series of typical chromatograms in Fig. 23 illustrates the effect of sample size.

4.7.4 Numerical results

In Table 19 are listed the experimental conditions and results, P_d being called P_2.

Table 19 Silver perchlorate in benzonitrile - experimental conditions and results

Expt. no.	Flow-rate $cm^3 min^{-1}$	Sample µmole	Column temp. deg C	10^3 P_2 atm	10^{-5} V_C $cm^3 mole^{-1}$	y
Packing PBN1, 90.3 cm, 183 µmole silver perchlorate, 2.03 µmole cm^{-1}						
1	9.7(5)	203	18.9	48.(5)	5.2(4)	1.06
Packing PBN1, 95.3 cm, 196 µmole silver perchlorate, 2.06 µmole cm^{-1}						
2	9.7(6)	79	18.9	-	-	-
3	9.7(1)	121	19.1	-	-	-
4	9.8(4)	162	19.3	48.(4)	3.9(4)	0.79
5	9.8(7)	204	19.2	50.(0)	4.4(2)	0.92
6	9.7(5)	24(6)	18.9	50.(0)	4.7(2)	0.99
7	9.7(8)	32(9)	18.8	50.(0)	5.3(1)	1.11
Packing PBN1, 172.6 cm, 345 µmole silver perchlorate, 2.00 µmole cm^{-1}						
8	9.8(7)	28(6)	18.8	48.(5)	4.4(8)	0.91
9	9.8(1)	32(7)	18.6	48.(6)	4.5(2)	0.92
Packing PBN1, 252.6 cm, 507 µmole silver perchlorate, 2.01 µmole cm^{-1}						
10	9.8(4)	41(2)	19.0	46.(9)	4.0(1)	0.78

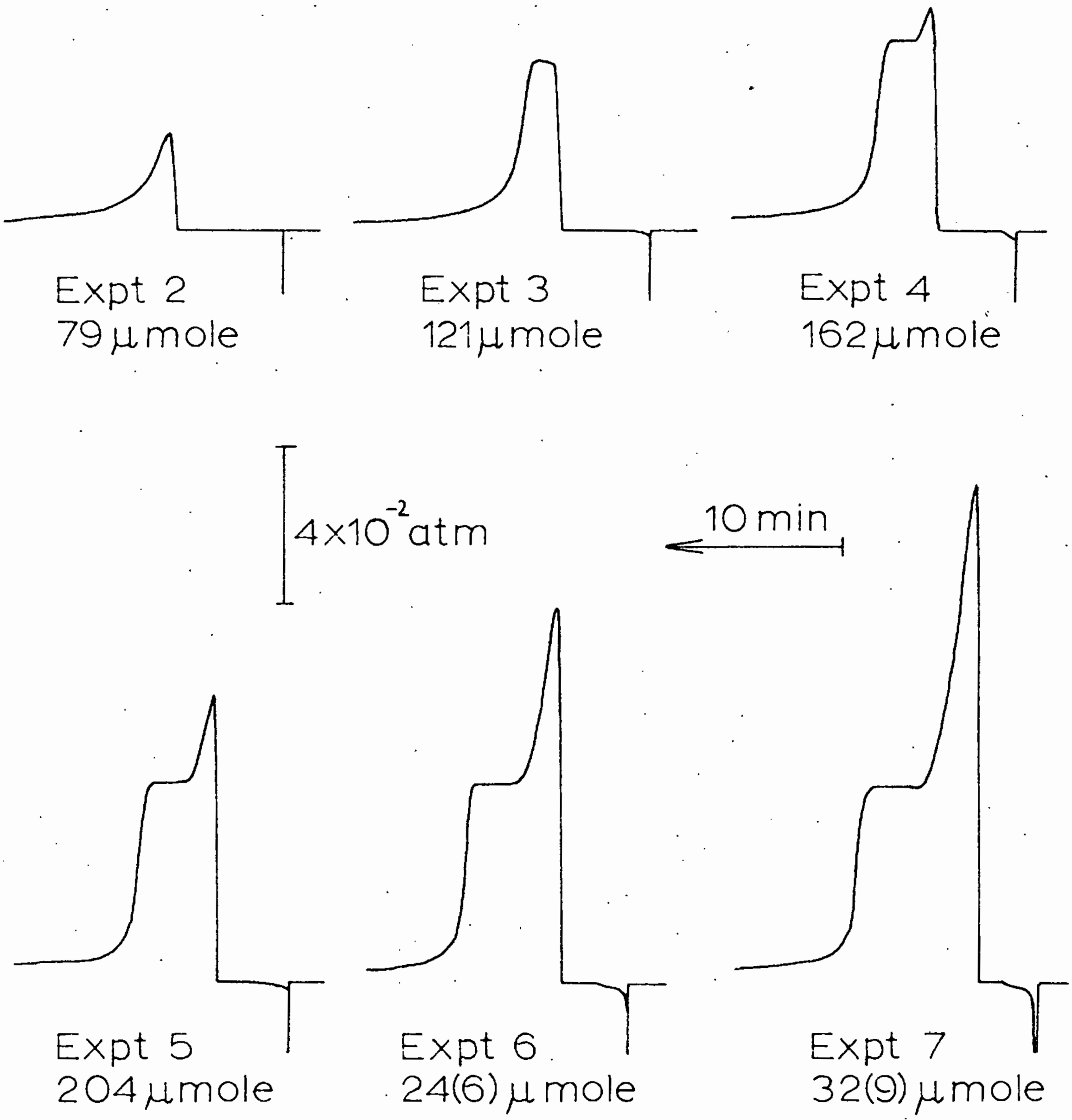

Figure 23. Silver perchlorate in benzonitrile —effect of sample size. Packing PBN1, flow-rate 9.7(1)-9.8(7) $cm^3 min^{-1}$, packing length 95.3cm, column temp. 18.8-19.3°C.

Table 19 (continued)

Expt. no.	Flow-rate $cm^3 min^{-1}$	Sample µmole	Column temp. deg C	10^3 P_2 atm	10^{-5} V_C $cm^3 mole^{-1}$	y
11	9.8(5)	49(3)	18.8	47.(1)	4.3(9)	0.86
Packing PBN2, 91.2 cm, 716 µmole silver perchlorate, 7.85 µmole cm^{-1}						
12	9.8(4)	61(6)	17.1	46.(6)	3.6(6)	0.72
Packing PBN2, 93.2 cm, 732 µmole silver perchlorate, 7.85 µmole cm^{-1}						
13	9.5(7)	41(6)	17.3	45.(2)	2.5(7)	0.49
14	9.8(5)	61(5)	18.4	49.(5)	3.3(7)	0.70
15	9.8(0)	83(7)	17.6	45.(7)	4.2(2)	0.81

y increases with sample size, and this may be the effect shown to a more marked degree by silver perchlorate in fenchone and ascribed to incomplete conversion of the salt in zone I to ammine, the degree of conversion increasing with increase in the ammonia pressure in zone I (see 4.9.4, p.84).

P_2 was determined at 17.1 to 19.3°C and has an average and standard deviation of 48.1×10^{-3} atm and 1.7×10^{-3} atm.

4.7.5 Comparison of Methods 1 and 2

Table 20 shows values of y calculated by different methods. The high and variable values of C and the discrepancies between columns 4 and 5 indicate impermanence of the initial absorption

Table 20 Silver perchlorate in benzonitrile - comparison of Methods 1 and 2

Expt. no.	Packing	10^3 C atm cm^{-1}	y by Method 1		t_e/t_h	y by Method 2	
			Measured sample	Effective sample		Ideal plateau	Approxi-mation
1	PBN1	3.5(4)	1.80	1.09	1.17	1.06	1.06
8	"	3.0(7)	1.33	0.94	1.18	0.93	0.91
9	"	3.2(7)	1.51	0.98	1.20	0.96	0.92
10	"	4.1(6)	1.60	0.81	1.16	0.79	0.79
11	"	3.8(1)	1.58	0.88	1.13	0.84	0.86
13	PBN2	3.0(6)	0.73	0.52	1.09	0.50	0.49
14	"	2.9(2)	0.95	0.72	1.07	0.71	0.70
15	"	3.2(0)	1.15	0.80	1.00	0.77	0.81

(see 2.6, p.22); good agreement between Methods 1 and 2 results from using the effective sample size in Method 1. t_e/t_h has an average value of 1.17 for Packing PBN1 and 1.05 for the richer Packing PBN2.

4.7.6 The dissociation pressure of the ammine responsible for initial absorption

The data necessary for calculating the dissociation pressure of the ammine responsible for initial absorption were not recorded, but this pressure must lie below 0.4×10^{-3} atm, the lowest pressure that can be detected by the katharometer (see 4.14.4, p.115).

4.7.7 Stoichiometric interpretation

The stoichiometric interpretation given in 4.6.8, p.76, for silver nitrate in benzonitrile applies also to the foregoing results for silver perchlorate in the same solvent. If there is no decomposition of the silver salt to an inert form, the following column reactions are indicated :

$$AgX + 1.5NH_3 \rightleftharpoons AgX(NH_3)_{1.5} \qquad p_{NH_3} < 0.4 \times 10^{-3} \text{ atm}$$

$$AgX(NH_3)_{1.5} + NH_3 \rightleftharpoons AgX(NH_3)_{2.5} \qquad p_{NH_3} = 48 \times 10^{-3} \text{ atm}$$

If decomposition takes place to the extent of about 30%, the equations may be

$$AgX + 2NH_3 \rightleftharpoons AgX(NH_3)_2 \qquad p_{NH_3} < 0.4 \times 10^{-3} \text{ atm}$$

$$AgX(NH_3)_2 + 1.5NH_3 \rightleftharpoons AgX(NH_3)_{3.5} \qquad p_{NH_3} = 48 \times 10^{-3} \text{ atm}$$

4.7.8 The effect of moisture

A drop of water was placed on the upstream end of Packing PBN1 (95.3 cm) after Expts. 2-7 and evaporated and eluted by the carrier gas. After this treatment the packing still gave an ammonia chromatogram with the usual plateau [48.(2) $\times 10^{-3}$ atm at 18.9°C], and it did therefore not contain silver perchlorate in the usual hygroscopic form.

4.8 Silver nitrate and silver perchlorate in benzonitrile

Packings NBN2 and PBN2 were mixed and a column was packed with 92.2 cm length of the mixture, containing 435 μmole of silver nitrate and 248 μmole of silver perchlorate.

Initially the chromatograms showed three plateaux (P_1, P_3, P_4) marked I, II, III in Fig. 24, Expt. 1, but after 13 days plateau III had disappeared (Fig. 24, Expt. 4). Table 21 shows the experimental conditions and results, the ages in column

Table 21 Silver nitrate and silver perchlorate in benzonitrile – experimental conditions and results

Expt. no.	Flow-rate cm^3 min^{-1}	Sample μmole	Column temp. deg C	10^3 P_d atm			$V_r^o - V_g$ cm^3			Age days
				P_1	P_3	P_4	Plat I	Plat II	Plat III	
1	9.7(8)	83(2)	16.6	70.(7)	37.(5)	27.(7)	123	159	197	0
2	9.7(8)	83(2)	16.6	70.(2)	37.(4)	27.(3)	121	154	197	0
3	9.8(2)	84(2)	16.3	67.(5)	36.(4)	26.(4)	125	162	197	1
4	9.6(1)	83(0)	17.7	75.(2)	39.(6)	-	102	171	-	13
5	9.7(7)	83(3)	16.9	72.(2)	40.(1)	-	109	171	-	22

11 being times after mixing of Packings NBN2 and PBN2. $V_r^o - V_g$ for the steepest part of the rear boundary of each plateau is reported instead of V_c and y, because it is doubtful what quantity of silver salt should be used for calculating V_c and y. The temperature ranges within which P_1, P_3 and P_4 were determined and the averages and standard deviations of these pressures are as follows :

P_1 16.3 - 17.7°C, 71.2 x 10^{-3} atm, 2.8 x 10^{-3} atm

P_3 16.3 - 17.7°C, 38.2 x 10^{-3} atm, 1.6 x 10^{-3} atm

P_4 16.3 - 16.6°C, 27.1 x 10^{-3} atm, 0.7 x 10^{-3} atm

The above value of P_1 is equal within the limits of experimental error to P_1 for silver nitrate in benzonitrile, but both plateaux II and III are lower than the plateau given by

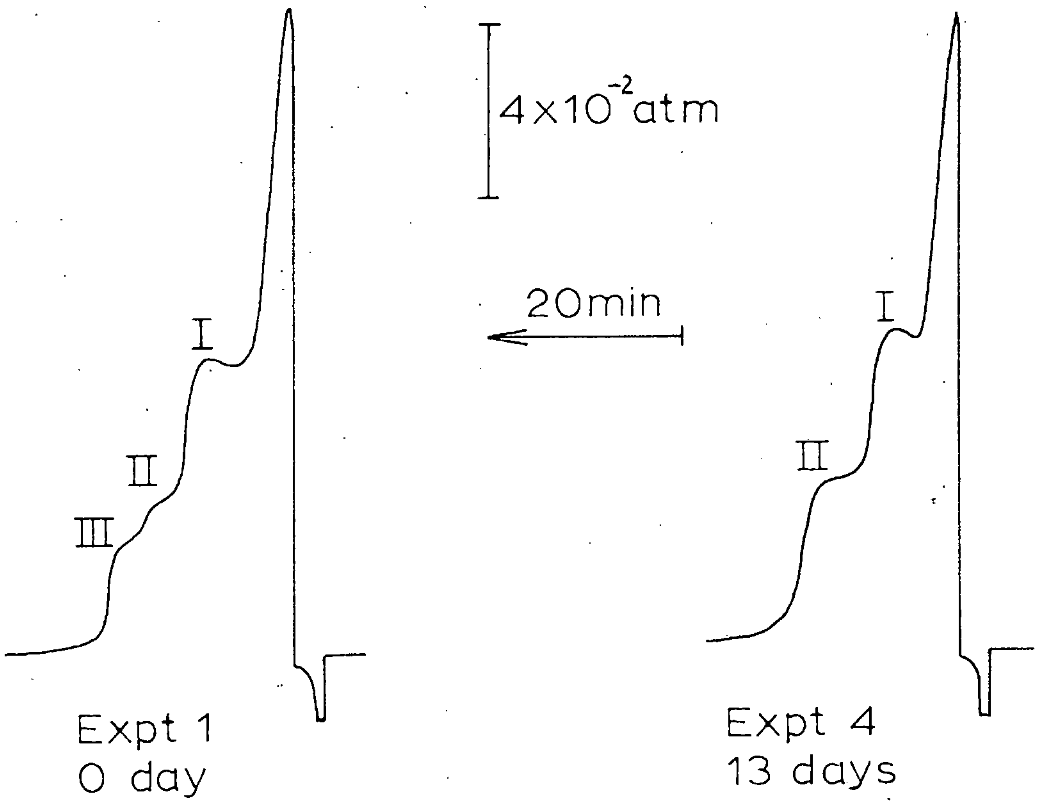

Figure 24. Silver nitrate and silver perchlorate in benzonitrile — effect of packing age. Column length 92.2 cm, flow-rate 9.6(1)-9.7(8) $cm^3 min^{-1}$, sample 83(0)-83(2) μmole, column temp. 16.6-17.7°C.

silver perchlorate in benzonitrile.

A possible explanation of these results is that a part of the precipitate present in Packing NBN2 persisted when the packings were mixed, while another part formed mixed crystals with the precipitate in Packing PBN2, and these then underwent further change.

4.9 Silver perchlorate in fenchone

After absorbing some ammonia initially, packings containing silver perchlorate in fenchone under certain conditions yield chromatograms having two plateaux, and show no changes on ageing.

Silver perchlorate in fenchone forms a white precipitate with ammonia and therefore acts as a heterogeneous fixed phase.

4.9.1 The packings

Table 22 gives details of the packings used. The leaner packings remained white, while the richer turned pale grey when the initial absorption of ammonia took place.

Table 22 Packings containing silver perchlorate in fenchone

Packing	Concentration μmole cm^{-3}	10^2 s cm^3 g^{-1}	Fenchone redistilled
PF1	125	3.00	Yes
PF2	127	3.00	No
PF3	138	3.00	Yes
PF4	601	3.00	Yes
PF5	810	3.00	Yes

4.9.2 The initial absorption

The following initial absorptions (moles of ammonia per mole of silver perchlorate) were measured :

Packing	PF2	> 1.1
"	PF4	1.9
"	PF5	2.1

4.9.3 The chromatograms

The chromatograms in Figs. 25 and 26 were obtained with the leanest packing (PF1) and show a single plateau (P_2), deformed by valley formation and rounding of the rear escarpment. They illustrate the effects of increasing sample size - conspicuous growth of the peak and moderate lengthening of the plateau.

The chromatograms shown in Figs. 27 and 28 were obtained with the richest packing (PF5) and differ in three respects from those in Figs. 25 and 26. Firstly, an increase in sample size has little effect on the peak but causes pronounced lengthening of the plateau. Secondly, a higher plateau (P_1, marked I) appears with larger samples. Thirdly, the P_2 plateau divides into two "plateaux" (marked II and III) of closely similar height. It is doubtful whether these two "plateaux" are due to different ammines - the division of the P_2 plateau is possibly a rate effect related to those described in 4.9.4. The P_2 plateau shows a marked slope and valley formation is pronounced in some chromatograms.

The effect of column length may be seen by comparing Expts. 4, 5, 6 (Fig. 25) with Expts. 9, 10, 11 (Fig. 26) and Expts. 25, 26, 29, 31, 34, 36 (Fig. 27) with Expts. 47, 49, 50, 51, 52, 53 (Fig. 28); that of silver perchlorate concentration by comparing Expts. 2, 6 (Fig. 25) with Expts. 24, 25 (Fig. 27) and Expts. 11, 12, 13, 15 (Fig. 26) with Expts. 47, 48, 49, 50 (Fig. 28). The influence of these variables is qualitatively in accordance with the predictions of 2.3, p.12.

4.9.4 Numerical results

In Table 23 are listed the experimental conditions and results for the P_2 plateau; where two values of P_2 are reported for an experiment, the first is for "plateau" II and the second for III.

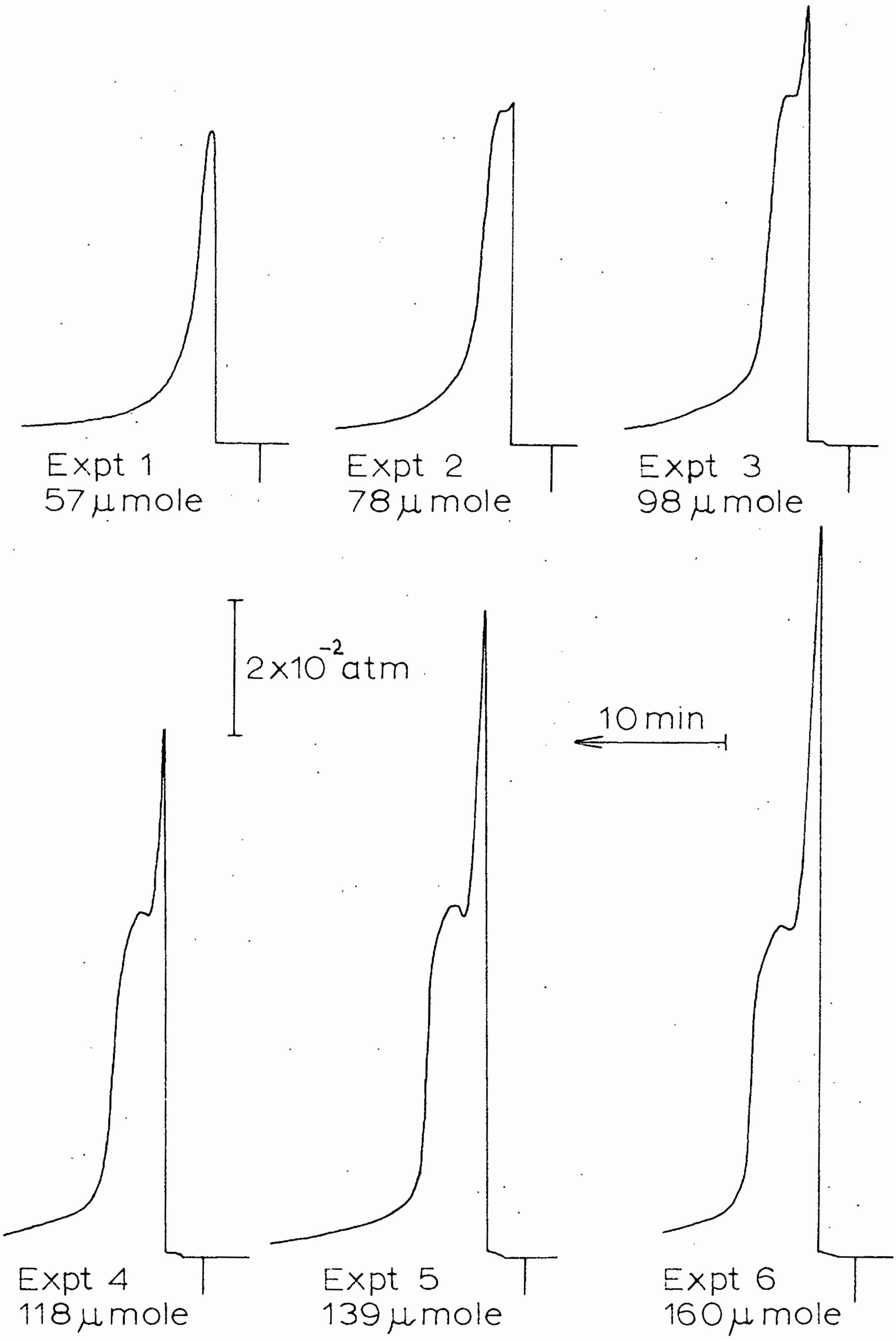

Figure 25. Silver perchlorate in fenchone —effect of sample size. Packing PF1, column length 90.0 cm, flow-rate 9.7(1)-9.8(0) $cm^3\ min^{-1}$, column temp. 23.0-24.0°C.

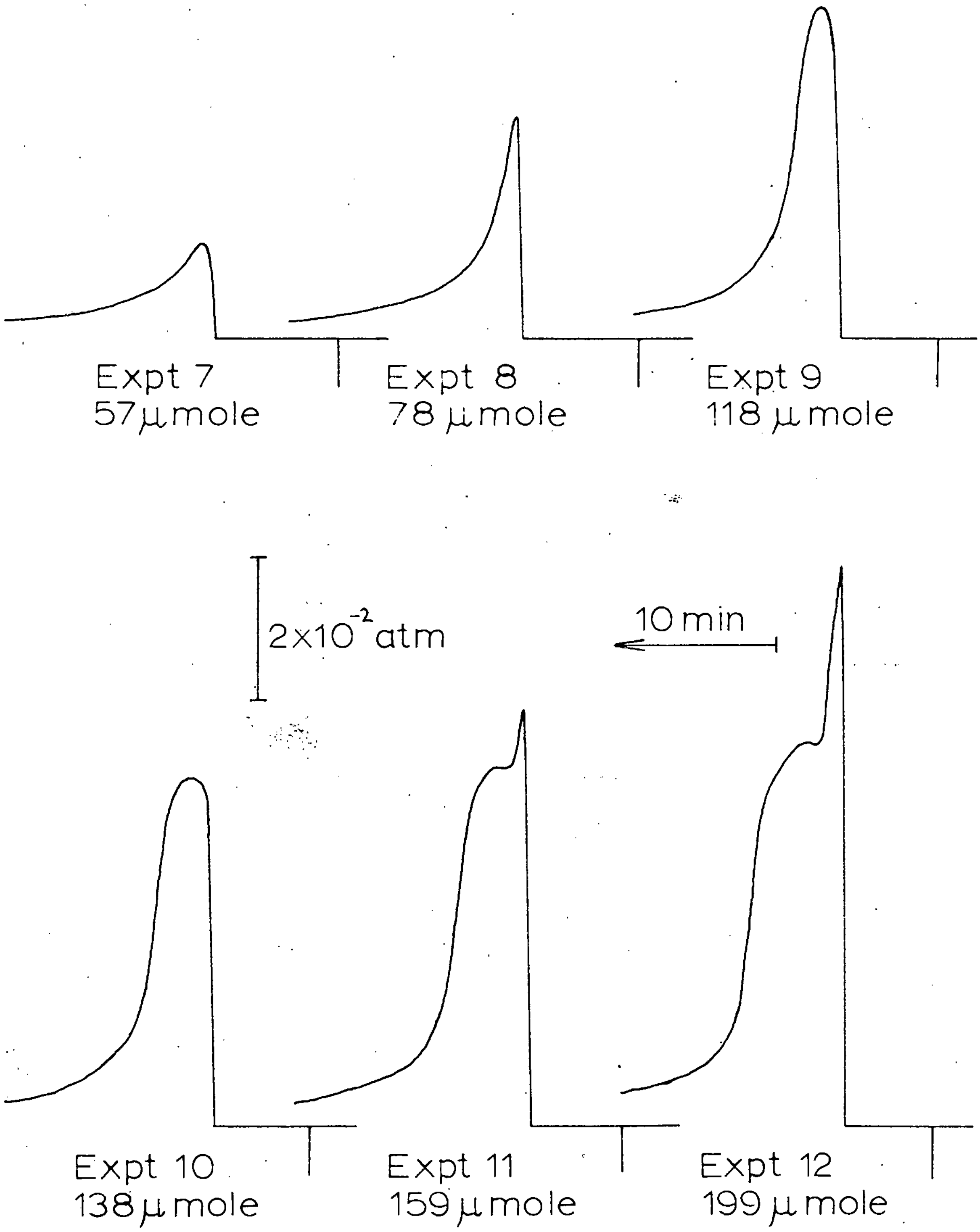

Figure 26. Silver perchlorate in fenchone —effect of sample size. Packing PF1, column length 171.0 cm, flow-rate 9.6(3)-9.7(7) $cm^3 min^{-1}$, column temp. 23.8-24.9°C.

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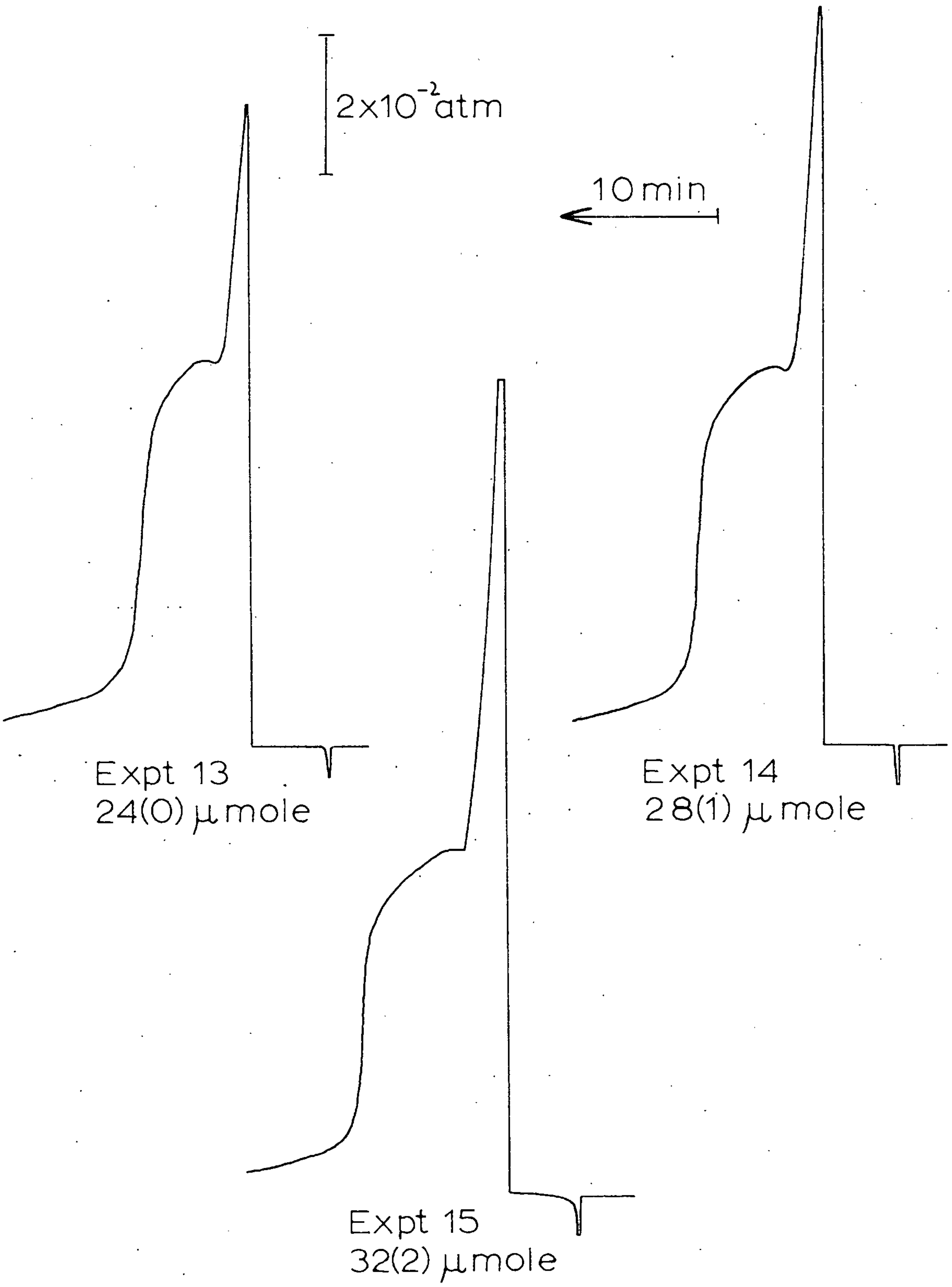

Figure 26, continued.

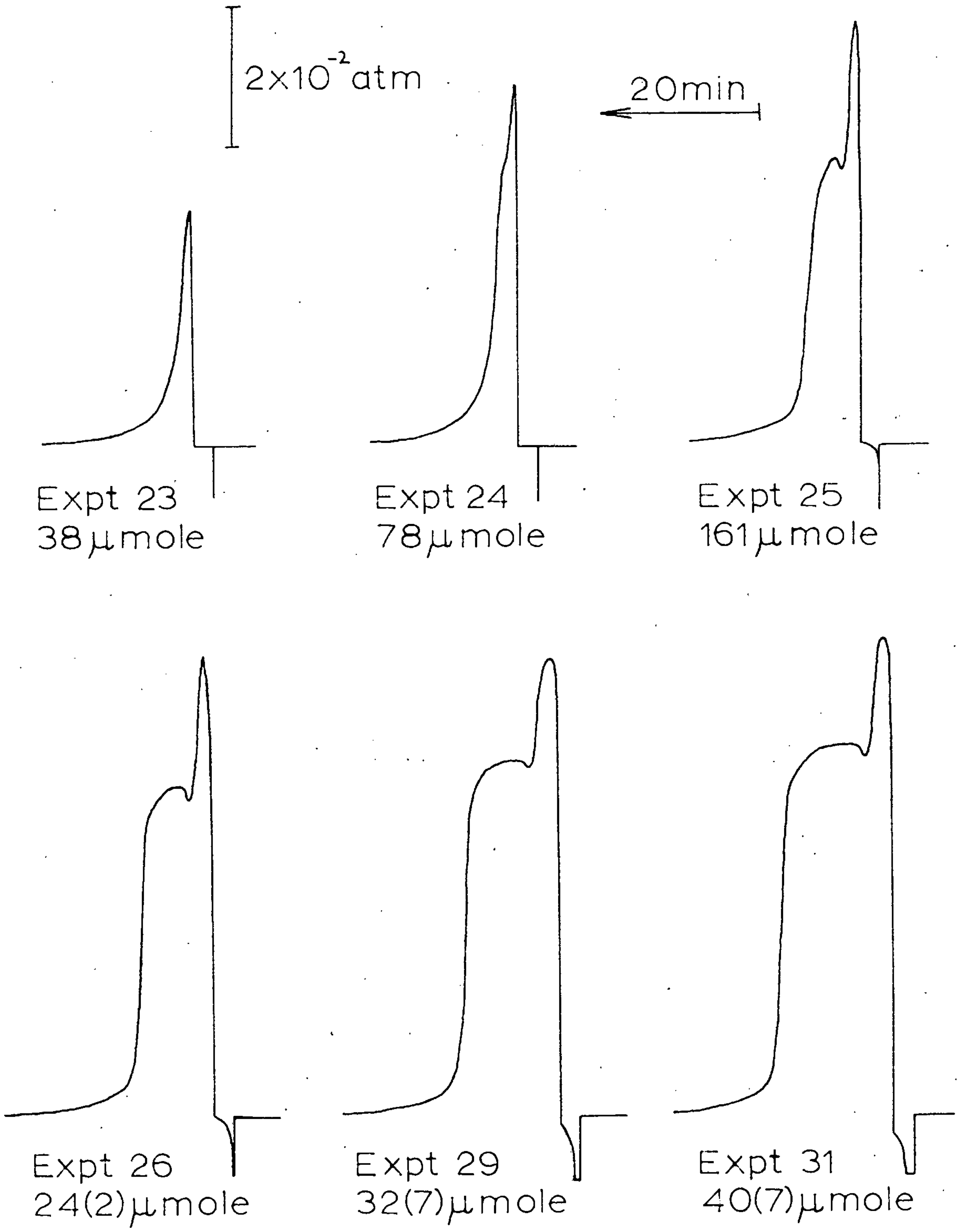

Figure 27. Silver perchlorate in fenchone —effect of sample size. Packing PF5, column length 90.1 cm, flow-rate 9.5(5)-9.7(8) $cm^3\,min^{-1}$, column temp. 20.3-22.7°C.

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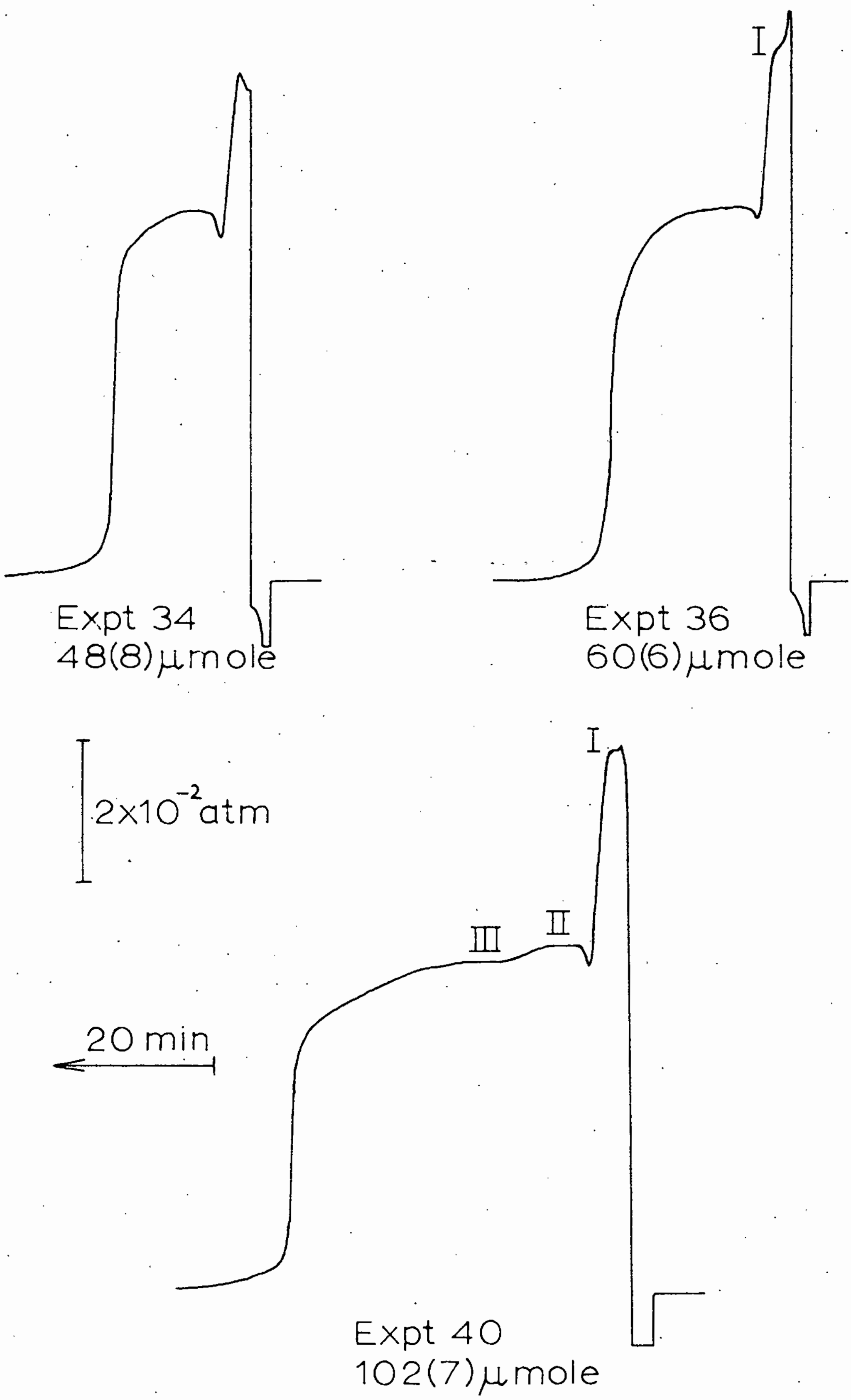


Figure 27, continued.

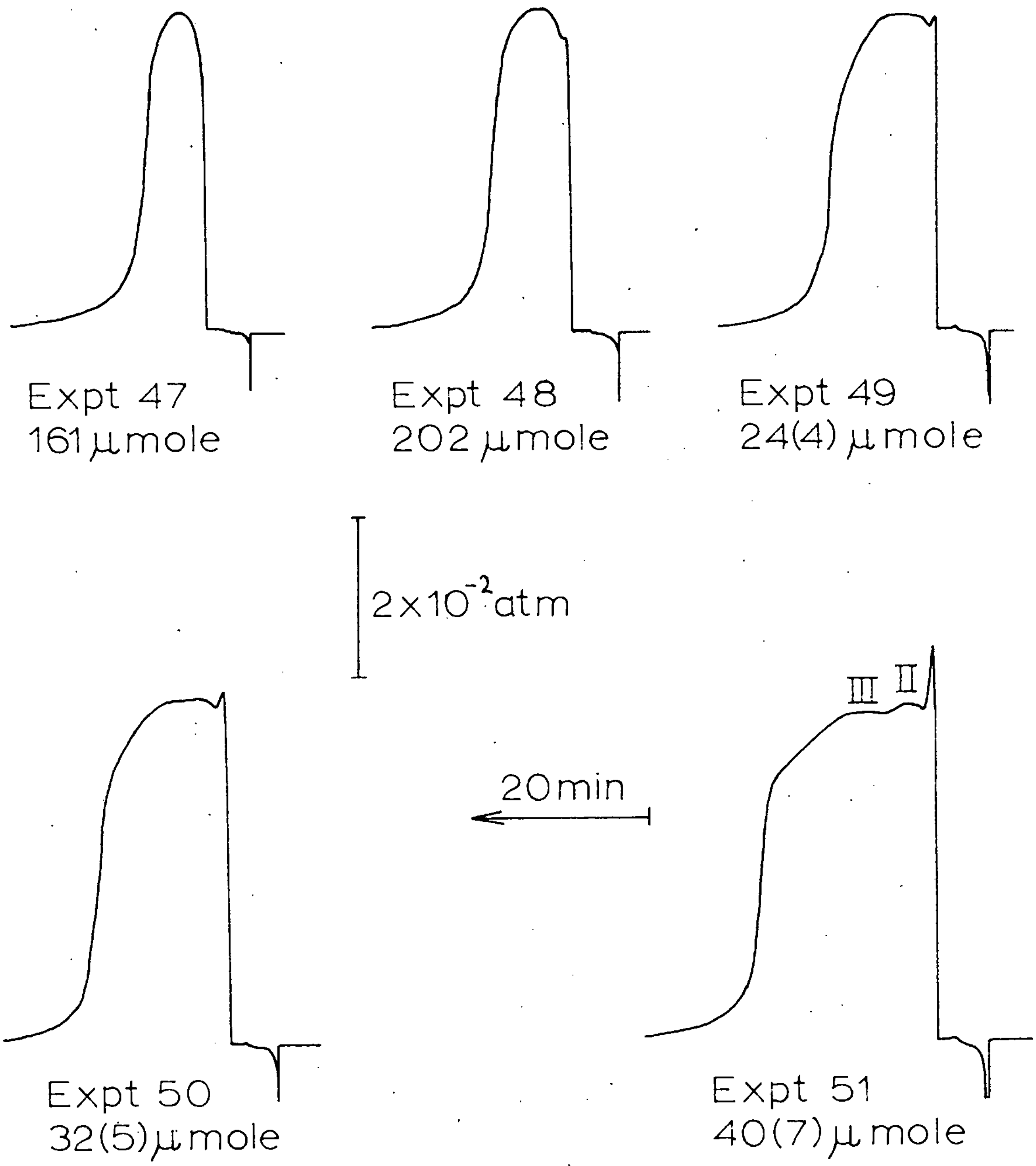


Figure 28. Silver perchlorate in fenchone — effect of sample size. Packing PF5, column length 171.1 cm, flow-rate 9.6(7)-9.8(4) $cm^3 min^{-1}$, column temp. 18.3-20.4°C.

Continued

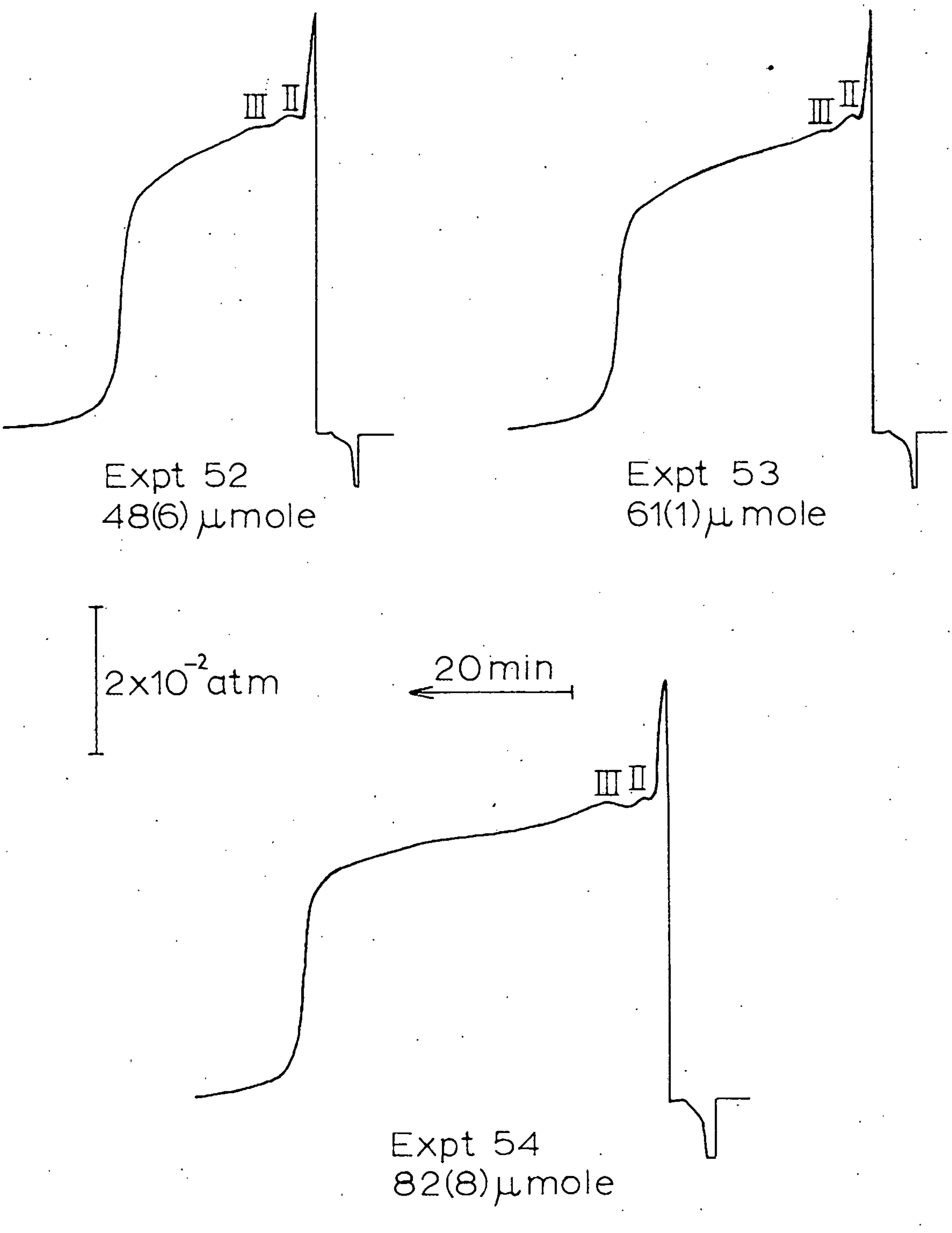


Figure 28, continued.

Table 23 Silver perchlorate in fenchone - experimental conditions and results for the lower plateau

Expt. no.	Flow-rate $cm^3\ min^{-1}$	Sample µmole	Column temp. deg C	$10^3\ P_2$ atm	$10^{-5}\ V_c$ $cm^3\ mole^{-1}$	y
Packing PF1, 90.0 cm, 178 µmole silver perchlorate, 1.98 $\mu mole\ cm^{-1}$						
1	9.7(6)	57	23.4	-	-	-
2	9.7(6)	78	23.7	50.(1)	2.8(4)	0.58
3	9.7(1)	98	23.9	52.(1)	3.1(1)	0.67
4	9.7(1)	118	24.0	51.(6)	3.4(8)	0.74
5	9.7(5)	139	23.9	52.(7)	3.7(6)	0.81
6	9.8(0)	160	23.0	49.(6)	4.1(8)	0.85
Packing PF1, 171.0 cm, 337 µmole silver perchlorate, 1.97 $\mu mole\ cm^{-1}$						
7	9.7(4)	57	24.9	-	-	-
8	9.6(3)	78	24.7	-	-	-
9	9.7(4)	118	24.2	-	-	-
10	9.6(3)	138	24.7	-	-	-
11	9.7(1)	159	24.4	50.(3)	2.9(2)	0.60
12	9.6(6)	199	24.7	53.(6)	3.2(1)	0.70
13	9.7(0)	24(0)	24.9	55.(2)	3.5(2)	0.80
14	9.7(5)	28(1)	24.8	54.(4)	3.7(8)	0.84
15	9.7(7)	32(2)	23.8	49.(7)	4.0(8)	0.83
Packing PF2, 88.6 cm, 178 µmole silver perchlorate, 2.01 $\mu mole\ cm^{-1}$						
16	8.2(2)	99	23.2	42.(3)	3.3(8)	0.59
17	8.2(8)	99	23.5	44.(3)	3.8(0)	0.69
18	8.4(8)	119	23.2	44.(9)	3.8(6)	0.71
19	8.7(5)	161	22.6	43.(9)	4.8(8)	0.89
Packing PF3, 90.0 cm, 196 µmole silver perchlorate, 2.18 $\mu mole\ cm^{-1}$						
20	9.7(6)	160	22.9	45.(6)	4.2(5)	0.80
21	9.7(0)	201	22.2	45.(1)	5.0(1)	0.93
22	9.7(4)	32(2)	23.7	47.(6)	6.8(9)	1.34
Packing PF5, 90.1 cm, 105(0) µmole silver perchlorate, 11.7 $\mu mole\ cm^{-1}$						
23	9.7(5)	38	20.9	-	-	-
24	9.7(5)	78	21.1	-	-	-
25	9.7(8)	161	20.3	40.(6)	0.9(2)	0.16
26	9.6(5)	24(2)	21.7	48.(0)	1.0(2)	0.20
27	9.6(6)	24(2)	23.1	54.(4)	0.9(3)	0.21
28	9.7(4)	32(6)	21.1	52.(6)	1.2(4)	0.27
29	9.6(2)	32(7)	21.1	51.(1)	1.2(4)	0.26
30	9.7(8)	40(6)	22.7	54.(7)	1.4(0)	0.32
31	9.8(3)	40(7)	21.7	53.(5)	1.4(6)	0.32
32	9.6(0)	40(8)	21.0	51.(2)	1.5(1)	0.32
33	9.6(5)	40(8)	22.7	55.(0)	1.4(1)	0.32
34	9.5(5)	48(8)	21.3	52.(3)	1.7(1)	0.37
35	9.7(7)	48(8)	22.2	55.(6)	1.6(5)	0.38
36	9.6(0)	60(6)	22.7	53.(3)	2.1(5)	0.47
37	9.7(5)	60(9)	21.6	54.(2)	2.1(6)	0.48
38	9.8(0)	61(2)	20.4	50.(5)	2.2(5)	0.47
39	9.5(8)	61(3)	20.8	52.(2)	2.3(4)	0.51
40	9.5(8)	102(7)	20.8	49.(9)		
				47.(7)	3.9(8)	0.79

Table 23 (continued)

Expt. no.	Flow-rate $cm^3\ min^{-1}$	Sample µmole	Column temp. deg C	10^3 P_2 atm	10^{-5} V_C $cm^3\ mole^{-1}$	y
Packing PF5, 90.0 cm, 108(5) µmole silver perchlorate, 12.1µmole cm^{-1}						
41	19.5(8)	162	19.2	32.(9)	0.8(2)	0.11
42	19.4(2)	24(4)	19.0	39.(4)	1.1(3)	0.19
43	19.4(0)	32(7)	19.3	41.(6)	1.4(2)	0.25
44	19.5(6)	40(9)	19.2	45.(5)	1.6(9)	0.32
45	19.4(8)	48(4)	21.7	50.(0)	1.7(6)	0.36
46	19.4(9)	60(7)	21.5	51.(0)	1.9(6)	0.41
Packing PF5, 171.1 cm, 202(0) µmole silver perchlorate, 11.8µmole cm^{-1}						
47	9.7(8)	161	19.2	-	-	-
48	9.8(4)	202	19.3	41.(7)	0.6(1)	0.11
49	9.7(9)	24(4)	18.3	41.(1)	0.7(6)	0.13
50	9.7(8)	32(5)	20.4	44.(9)	0.9(0)	0.17
51	9.7(7)	40(7)	20.3	43.(6) 42.(6)	1.1(3)	0.20
52	9.6(7)	48(6)	20.3	44.(6) 42.(8)	1.3(0)	0.23
53	9.7(7)	61(1)	19.8	44.(3) 42.(2)	1.6(9)	0.30
54	9.8(3)	82(8)	19.3	42.(8) 42.(0)	2.3(5)	0.41
55	19.5(8)	41(4)	18.4	37.(9) 35.(7)	1.3(0)	0.19
56	19.5(8)	61(9)	18.3	38.(3) 35.(2)	1.8(3)	0.27
57	19.6(3)	83(2)	18.2	39.(3) 35.(6)	2.6(3)	0.39

P_2 decreases with increase in flow-rate, an effect which is possibly due to the slowness of decomposition responsible for valley formation, the ammonia from the slowly decomposing ammine being swept away before its partial pressure builds up to the equilibrium value of P_2 .

V_c and y increase with increase in sample size and this effect is pronounced with the richest packing (PF5), which has small fractional values of y for small samples. This indicates that only a fraction of the silver salt in the column is converted to the P_2 ammine, and that this fraction increases with the increase of ammonia pressure in zone I (see 2.3.1, p.13) resulting from an increase in sample size.

Table 24 shows values of P_d (called P_1), V_c and y for plateau I, the value 1 being assumed for t_e/t_h.

Table 24 Silver perchlorate in fenchone - results for the higher plateau

Expt. no.	10^3 P_1 atm	10^{-5} V_c cm^3 $mole^{-1}$	y
36	76.(7)	0.11(3)	0.036
37	75.(1)	0.12(1)	0.038
38	71.(6)	0.12(3)	0.037
39	74.(0)	0.11(1)	0.034
40	77.(2)	0.11(6)	0.037

In the experiments with the lower flow-rates (< 10 cm^3 min^{-1}), P_2 lies between 40.(6) x 10^{-3} atm and 55.(6) x 10^{-3} atm, the range of temperature being 18.3 to 24.9°C. P_1 was measured between 20.4 and 22.7°C and has an average and standard deviation of 74.9 x 10^{-3} atm and 2.3 x 10^{-3} atm.

4.9.5 Comparison of Methods 1 and 2

Table 25 shows values of y calculated by different methods. The high and variable values of C and the discrepancies between columns 4 and 5 indicate impermanence of the initial absorption (see 2.6, p.22); good agreement between Methods 1 and

Table 25 Silver perchlorate in fenchone - comparison of Methods 1 and 2

Expt. no.	Packing	10^3 C atm cm^{-1}	y by Method 1		t_e/t_h	y by Method 2	
			Measured sample	Effective sample		Ideal plateau	Approxi-mation
16	PF2	3.0(6)	0.85	0.59	1.19	0.59	0.59
17	"	2.6(7)	0.88	0.72	1.21	0.70	0.69
29	PF5	2.4(1)	0.35	0.27	1.05	0.27	0.26
30	"	2.8(3)	0.40	0.31	1.02	0.31	0.32
31	"	2.8(1)	0.42	0.33	1.03	0.32	0.32
32	"	2.8(1)	0.42	0.33	1.05	0.32	0.32
33	"	2.7(8)	0.43	0.34	1.04	0.32	0.32
34	"	2.7(9)	0.48	0.38	1.04	0.37	0.37
35	"	2.7(6)	0.48	0.39	1.03	0.38	0.38
37	"	2.9(0)	0.59	0.50	1.05	0.49	0.48
38	"	2.8(0)	0.59	0.46	1.00	0.46	0.47

Table 25 (continued)

Expt. no.	Packing	10^3 C atm cm^{-1}	y by Method 1		t_e/t_h	y by Method 2	
			Measured sample	Effective sample		Ideal plateau	Approximation
48	PF5	2.7(2)	0.14	0.11	1.04	0.11	0.11
49	"	2.6(0)	0.16	0.13	1.03	0.13	0.13
50	"	2.6(3)	0.20	0.17	1.01	0.16	0.17

2 results from using the effective sample size in Method 1. For the leaner packing PF2, t_e/t_h has an average value of 1.20; this was used in calculating V_c for Packings PF1, PF2 and PF3. For Packing PF5, t_e/t_h has an average value of 1.03.

4.9.6 The dissociation pressure of the ammine responsible for initial absorption

The data necessary for calculating the dissociation pressure of the ammine responsible for initial absorption were not recorded, but this pressure must lie below 0.4×10^{-3} atm, the lowest pressure that can be detected by the katharometer (see 4.14.4, p.115).

4.9.7 Stoichiometric interpretation

The values of the initial absorption and the higher values of y in Table 23 indicate the equations

$$AgX + 2NH_3 \rightleftharpoons AgX(NH_3)_2 \qquad p_{NH_3} < 0.4 \times 10^{-3}\,\text{atm}$$

$$AgX(NH_3)_2 + NH_3 \rightleftharpoons AgX(NH_3)_3 \qquad p_{NH_3} \sim 50 \times 10^{-3}\,\text{atm}$$

for the column reactions, but one value of y, that for Expt. 22, suggests that the coefficient of NH_3 in the second equation may be too low. Plateau I is too poorly developed to yield any stoichiometric information.

4.9.8 The effect of moisture

A drop of water was placed on the upstream end of Packing PF1 after Expts. 1-15 and evaporated and eluted by the carrier gas. After this treatment the packing still gave an ammonia chromatogram with the usual plateau [46.(3) x 10^{-3} atm at 23.5°C and flow-rate 9.8(1) cm^3 min^{-1}], and it did therefore not contain silver perchlorate in the usual hygroscopic form.

4.10 Silver perchlorate in fenchone and benzyl cyanide

Fenchone and benzyl cyanide are miscible in all proportions and some experiments were made with packings containing silver perchlorate in mixtures of these solvents. The salt was dissolved in the separate solvents (138.0 μmole cm^{-3} in fenchone, 138.3 μmole cm^{-3} in benzyl cyanide) and the solutions were mixed in different proportions for the packings, which had $s = 0.0300$ cm^3 g^{-1} . All the packings were white when prepared, but those containing less than 70.1 mole % fenchone in the solvent turned a permanent pale mauve soon after preparation and before ammonia was injected. The initial absorption was not measured.

Fig. 29 shows the effect of solvent composition and Fig. 30 that of sample size for 41.7 mole % fenchone in the solvent. The chromatograms show a low and a high plateau, of which the latter changes in shape and height as the solvent composition changes from 100 to 41.7 mole % fenchone.

Table 26 gives the experimental conditions and numerical results, the value 1 being assumed for t_e/t_h for both plateaux; the packings are distinguished by the molar percentage of fenchone in the solvent. This percentage is followed by the age of the solutions when the packing was prepared, and the age of the packing is listed in column 11. These ages are given because a solution of silver perchlorate in benzyl cyanide changes with time (see 4.5.7, p.68). The headings "High" and "Low" in columns 5-10 refer to the high and low plateaux.

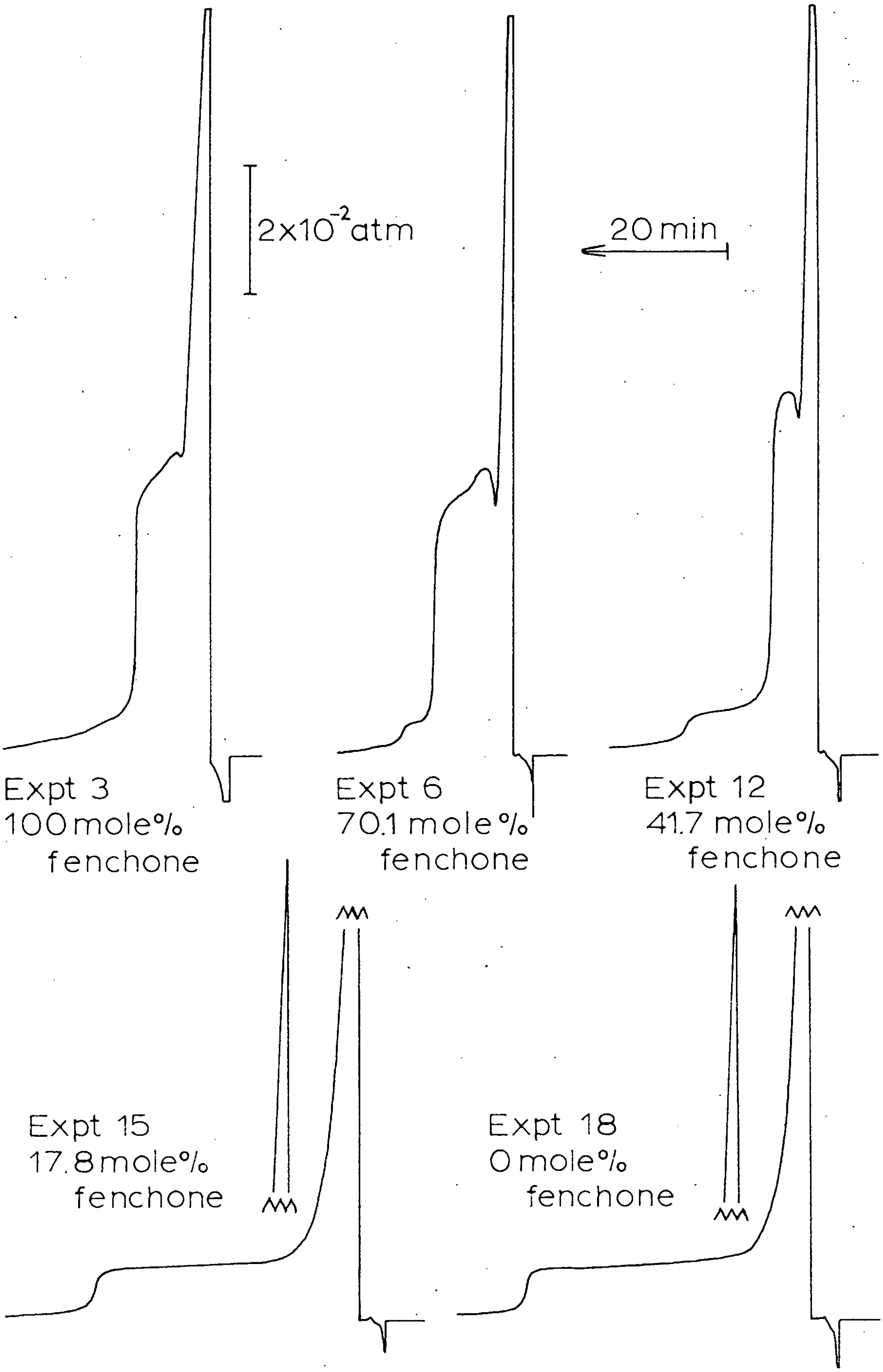


Figure 29. Silver perchlorate in fenchone and benzyl cyanide — effect of solvent composition. Column length 86.3-90.0 cm, flow-rate 9.7(4)-9.8(3) $cm^3 min^{-1}$, sample 32(2)-33(0) μmole, column temp. 19.6-23.7 °C.

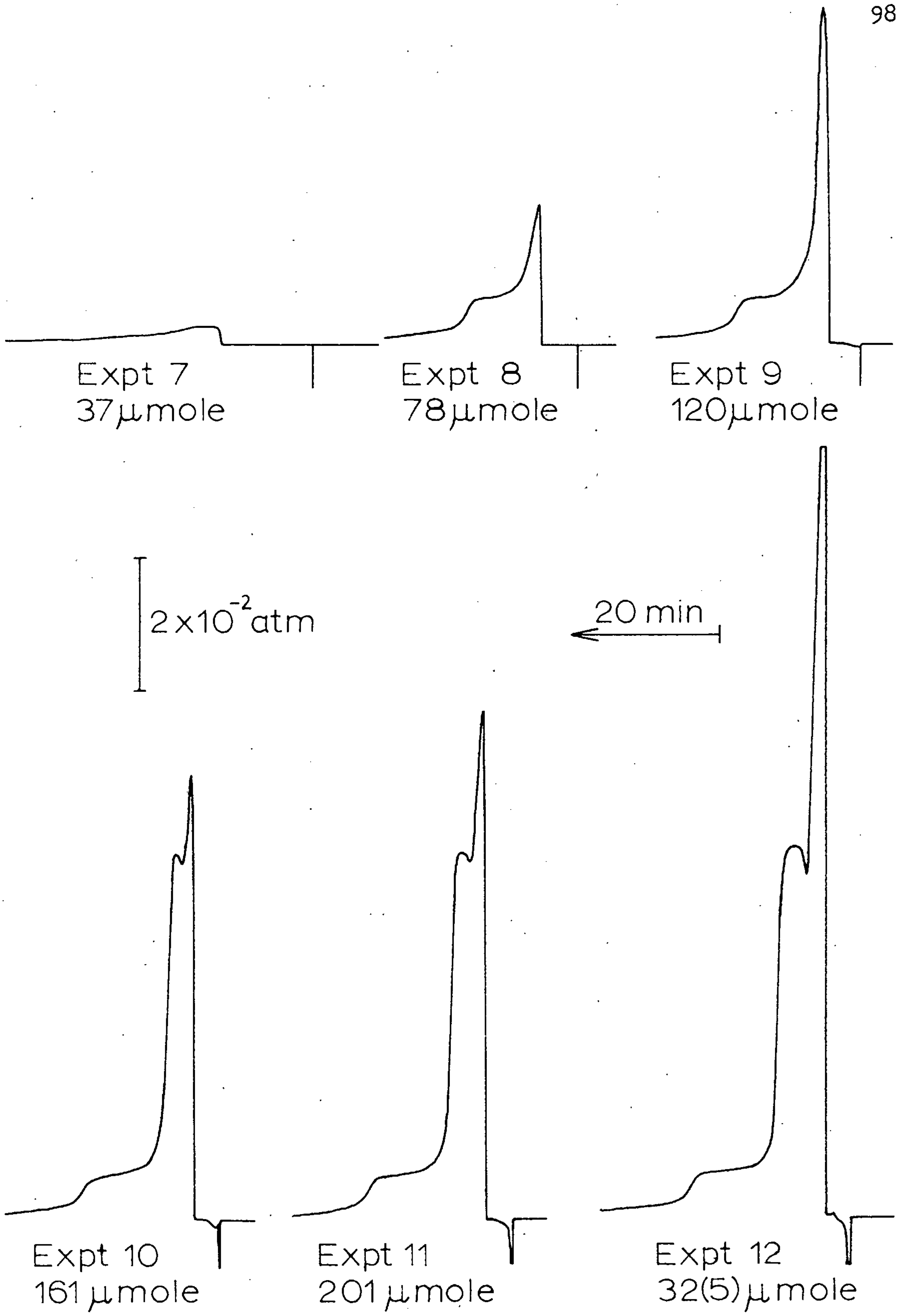


Figure 30. Silver perchlorate in fenchone and benzyl cyanide—effect of sample size. 41.7 mole% fenchone, column length 86.3 cm, flow-rate 9.7(2) -9.8(2) $cm^3 min^{-1}$, column temp. 21.2-23.3°C.

Table 26 Silver perchlorate in fenchone and benzyl cyanide - experimental conditions and results

Expt. no.	Flow-rate cm^3 min^{-1}	Sample µmole	Column temp. deg C	10^3 P_d atm		10^{-5} V_c cm^3 $mole^{-1}$		y		Age days
				High	Low	High	Low	High	Low	
100 mole% fenchone, 8 days, 90.0 cm, 196 µmole silver perchlorate, 2.18 µmole cm^{-1}										
1	9.7(6)	160	22.9	45.(6)	-	3.3(7)	-	0.63	-	1
2	9.7(0)	201	22.2	45.(1)	-	3.9(8)	-	0.74	-	1
3	9.7(4)	32(2)	23.7	47.(6)	-	5.6(7)	-	1.11	-	0
70.1 mole% fenchone, 20 days, 94.2 cm, 197 µmole silver perchlorate, 2.09 µmole cm^{-1}										
4	9.7(7)	163	20.9	51.(4)	7.1(3)	3.3(5)	6.1(0)	0.72	0.18(0)	1
5	9.7(0)	204	20.4	50.(7)	7.0(4)	4.1(1)	6.8(5)	0.87	0.20(0)	1
6	9.8(3)	33(0)	19.6	45.(0)	6.3(3)	6.1(0)	7.8(7)	1.14	0.20(7)	1
41.7 mole% fenchone, 7 days, 86.3 cm, 197 µmole silver perchlorate, 2.28 µmole cm^{-1}										
7	9.7(2)	37	23.3	-	-	-	-	-	-	1
8	9.7(8)	78	22.8	-	7.8(0)	-	6.6(0)	-	0.21(2)	1
9	9.7(3)	120	22.2	-	7.5(3)	-	7.3(5)	-	0.22(8)	1
10	9.8(0)	161	21.2	55.(9)	7.6(2)	2.9(2)	8.2(7)	0.68	0.26(0)	1
11	9.8(0)	201	21.8	56.(1)	7.5(8)	3.3(5)	8.6(2)	0.77	0.26(9)	0
12	9.8(2)	32(5)	21.7	56.(3)	7.4(4)	4.0(6)	9.4(9)	0.94	0.29(1)	0
17.8 mole% fenchone, 17 days, 89.0 cm, 195 µmole silver perchlorate, 2.19 µmole cm^{-1}										
13	9.7(4)	161	21.0	-	7.5(3)	-	18.(3)	-	0.57	3
14	9.7(7)	200	22.4	-	8.4(2)	-	17.(4)	-	0.60	2
15	9.7(7)	32(2)	22.7	-	8.3(7)	-	18.(9)	-	0.65	2
0 mole% fenchone, 6 days, 90.0 cm, 194 µmole silver perchlorate, 2.16 µmole cm^{-1}										
16	9.6(8)	160	22.1	-	7.9(4)	-	18.(9)	-	0.62	4
17	9.7(3)	200	23.7	-	9.0(5)	-	18.(2)	-	0.68	3
18	9.6(8)	32(2)	23.7	-	8.3(5)	-	20.(3)	-	0.70	3

It is evident from the values of P_d that the low plateau is plateau II (7.7×10^{-3} atm) of the system silver perchlorate - benzyl cyanide; V_c and y for this plateau increase with increasing mole fraction of benzyl cyanide in the solvent, showing that an increasing fraction of the silver salt is present in the same form as in pure benzyl cyanide. The behaviour of the high plateau is more complicated - P_d increases and V_c and y first increase and then decrease with increase in the mole fraction of benzyl cyanide; these changes indicate that different ammines are responsible for the high plateau at different compositions of the solvent. Plateau I [50.(4) x 10^{-3} atm] of the silver perchlorate-benzyl cyanide system is not shown by the packings with 0 mole% and 17.8 mole % fenchone (Fig. 29, Expts. 18, 15) and is therefore not the high plateau shown by the packings with 41.7 mole% and 70.1 mole% fenchone (Fig. 29, Expts. 12, 6).

4.11 Silver perchlorate in tetralin

After absorbing some ammonia initially, packings containing silver perchlorate in tetralin produce chromatograms with a single plateau (P_3) and show no changes on ageing.

Silver perchlorate in tetralin forms a white precipitate with ammonia and therefore acts as a heterogeneous fixed phase.

4.11.1 The packings

Table 27 gives details of the packings used.

Table 27 Packings containing silver perchlorate in tetralin

Packing	Concentration μmole cm^{-3}	10^2 s cm^3 g^{-1}	Tetralin manufacturer	Tetralin redistilled
PT1	135	3.00	L.L.& Co.	No
PT2	151	3.57	L.L.& Co.	No
PT3	185	3.00	R.-de H.	Yes
PT4	1120	1.05	R.-de H.	Yes
PT5	2470	1.00	R.-de H.	Yes

The colour of a new packing was grey, but this changed to white or pale cream under the action of ammonia.

4.11.2 The initial absorption

The following initial absorptions (moles of ammonia per mole of silver perchlorate) were measured :

Packing	PT1	2.1
"	PT4	1.9
"	PT5	> 1.7

4.11.3 The chromatograms

The chromatograms in Fig. 31 were obtained with one of the leaner packings (PT3) and show a plateau with a very indefinite rear boundary, a feature which may be due to the wide departure of the ammonia-tetralin system from Henry's law (see 4.3, p.45) and the consequent tailing of ammonia peaks given by the pure solvent.

In the experiments with a rich packing (PT4) which gave the chromatograms of Fig. 32, the retentive effect of the solvent was reduced by using a low ratio of solvent to support. The plateau has a steep rear boundary, but slopes somewhat; increase in sample size causes both lengthening of the plateau and growth of the peak.

4.11.4 Numerical results

In Table 28 the experimental conditions and results are recorded.

Table 28 Silver perchlorate in tetralin - experimental conditions and results

Expt. no.	Flow-rate $cm^3 min^{-1}$	Sample µmole	Column temp. deg C	10^3 P_3 atm	10^{-5} V_c cm^3 $mole^{-1}$	y
Packing PT1, 88.2 cm, 189 µmole silver perchlorate, 2.14 µmole cm^{-1}						
1	7.3(7)	201	23.2	40.(2)	4.5(5)	0.75
Packing PT2, 171.0 cm, 488 µmole silver perchlorate, 2.85 µmole cm^{-1}						
2	9.7(5)	160	21.6	29.(7)	2.6(9)	0.33
3	9.7(1)	180	24.0	34.(1)	2.5(0)	0.35
4	9.4(5)	200	23.7	35.(4)	2.7(3)	0.40
5	9.6(5)	200	23.0	34.(3)	2.7(7)	0.39
6	9.6(0)	200	22.9	32.(8)	2.8(3)	0.38
7	9.7(1)	201	24.0	33.(4)	2.7(3)	0.37
Packing PT3, 90.0 cm, 274 µmole silver perchlorate, 3.04 µmole cm^{-1}						
8	9.6(6)	32(3)	24.0	41.(1)	6.1(7)	1.04
Packing PT3, 171.0 cm, 505 µmole silver perchlorate, 2.95 µmole cm^{-1}						
9	9.8(2)	24(2)	22.1	-	-	-
10	9.6(7)	32(4)	24.3	39.(1)	5.9(0)	0.95
11	9.7(8)	40(7)	23.4	40.(6)	6.3(4)	1.06
12	9.7(6)	48(7)	23.7	39.(6)	6.6(6)	1.08
13	9.6(9)	60(9)	24.0	38.(8)	6.9(3)	1.10
14	34.0	40(6)	22.9	30.(3)	7.0(9)	0.89

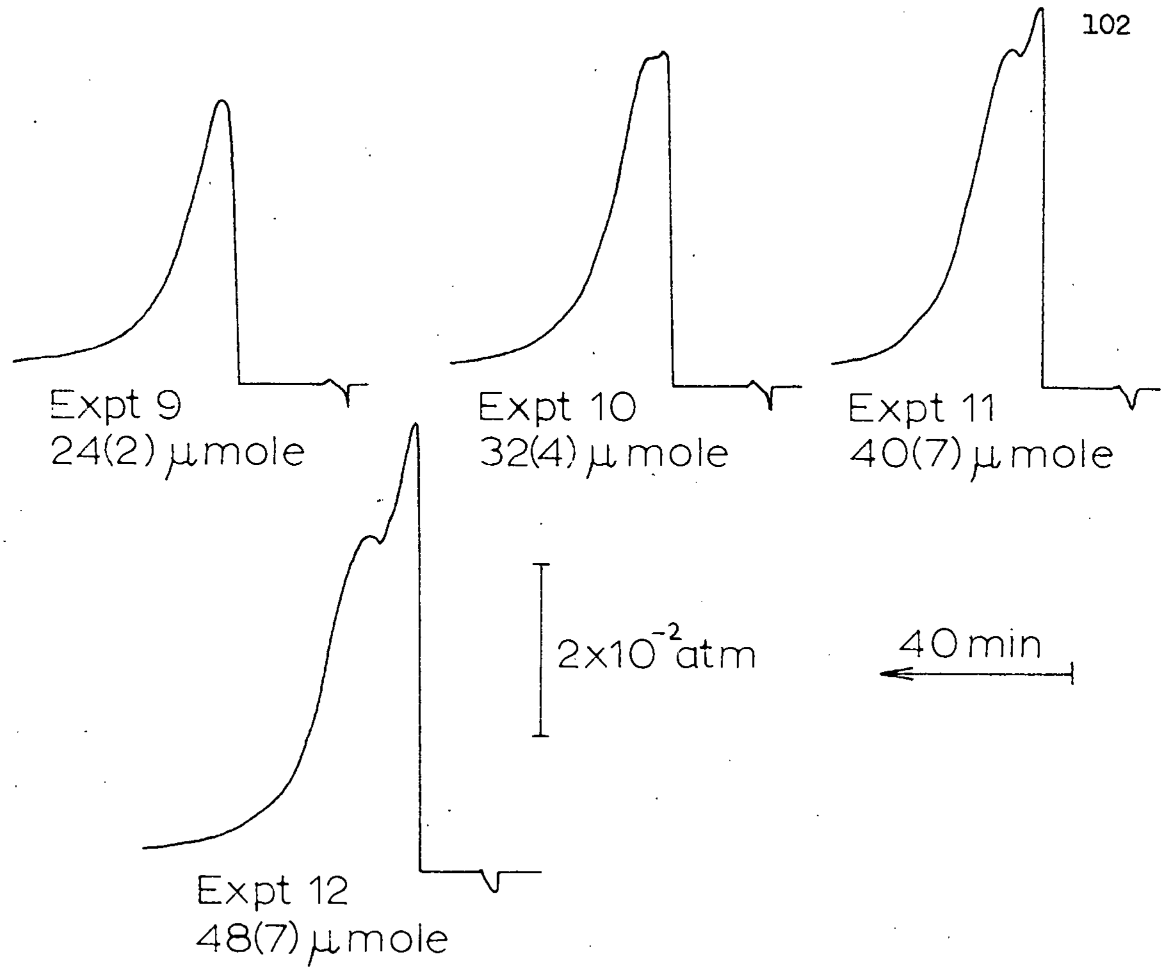


Figure 31. Silver perchlorate in tetralin—effect of sample size. Packing PT3, column length 171.0 cm, flow-rate 9.6(7)-9.8(2) $cm^3 min^{-1}$, column temp. 22.1-24.3°C.

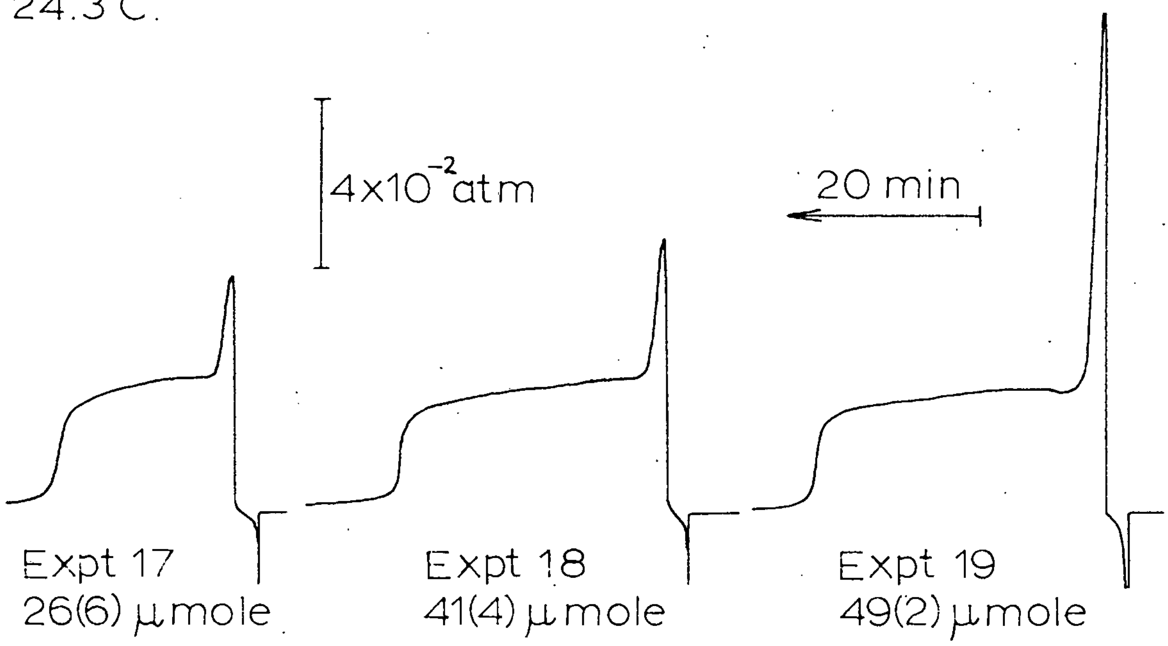


Figure 32. Silver perchlorate in tetralin—effect of sample size. Packing PT4, column length 81.6 cm, flow-rate 9.7(1)-9.9(5) $cm^3 min^{-1}$, column temp. 17.0-17.8°C.

Table 28 (continued)

Expt. no.	Flow-rate $cm^3 min^{-1}$	Sample µmole	Column temp. deg C	10^3 P_3 atm	10^{-5} V_c cm^3 $mole^{-1}$	y
15	34.0	40(6)	22.9	31.(5)	6.9(3)	0.90
16	34.2	40(6)	22.7	31.(1)	7.0(9)	0.91
Packing PT4, 81.6 cm, 482 µmole silver perchlorate, 5.92 µmole cm^{-1}						
17	9.7(8)	26(6)	17.8	32.(8)	3.7(4)	0.51
18	9.7(1)	41(4)	17.0	31.(9)	5.4(5)	0.73
19	9.9(5)	49(2)	17.2	29.(4)	6.0(5)	0.75
Packing PT5 82.5 cm, 101(4) µmole silver perchlorate, 12.3 µmole cm^{-1}						
20	9.7(3)	32(9)	18.7	35.(4)	1.9(2)	0.28
21	9.8(0)	62(0)	19.4	39.(1)	3.1(0)	0.51
22	33.0	61(6)	19.0	37.(9)	3.1(5)	0.50

V_c and y increase with increase in sample size, and this may be due to incomplete conversion of the silver salt in zone I to the plateau-forming ammine (cf. 4.9.4, p.84).

P_3, having an average and standard deviation of 35.2×10^{-3} atm and 3.9×10^{-3} atm for temperatures of 17.0 to 24.3° C, is more variable than most of the values of P_d determined for other systems.

4.11.5 Comparison of Methods 1 and 2

Table 29 shows values of y calculated by different methods. The high values of C and the discrepancies between columns 3 and 4 indicate impermanence of the initial absorption (see 2.6, p.22); good agreement between Methods 1 and 2 results

Table 29 Silver perchlorate in tetralin - comparison of Methods 1 and 2

Expt. no.	10^3 C atm cm^{-1}	y by Method 1		t_e/t_h	y by Method 2	
		Measured sample	Effective sample		Ideal plateau	Approximation
18	2.6(6)	0.87	0.73	0.94	0.71	0.73
19	2.7(1)	0.97	0.78	0.98	0.76	0.75

from using the effective sample size in Method 1. t_e/t_h has an average value of 0.96; this is for Packing PT4 only, and for the other packings, which differ widely from PT4 in silver perchlorate concentration, the value 1 is assumed for t_e/t_h.

4.11.6 The dissociation pressure of the ammine responsible for initial absorption

The data necessary for calculating the dissociation pressure of the ammine responsible for initial absorption were not recorded, but this pressure must lie below 0.4×10^{-3} atm, the lowest pressure that can be detected by the katharometer (see 4.14.4, p.115).

4.11.7 Stoichiometric interpretation

The values of the initial absorption and the higher values of y in Table 28 indicate the following equations for the column reactions :

$$AgX + 2NH_3 \rightleftharpoons AgX(NH_3)_2 \qquad p_{NH_3} < 0.4 \times 10^{-3} \text{ atm}$$

$$AgX(NH_3)_2 + NH_3 \rightleftharpoons AgX(NH_3)_3 \qquad p_{NH_3} = 35 \times 10^{-3} \text{ atm}$$

4.11.8 The effect of moisture

A drop of water was placed on the upstream end of Packing PT5 after Expts. 20-22 and evaporated and eluted by the carrier gas. After this treatment the packing still gave an ammonia chromatogram with the usual plateau [38.(9) $\times 10^{-3}$ atm at 19.7°C] and it did therefore not contain silver perchlorate in the usual hygroscopic form.

4.12 Silver nitrate in m-toluidine

The chromatography of ammonia on m-toluidine containing silver nitrate in solution is true gas-liquid chromatography, since no precipitate is formed. A packing containing such a solution does not absorb ammonia initially and the chromatograms are therefore suitable for determining the calibration factor of the detector. The chromatograms have no plateau and this, together with the absence of initial absorption, shows that the m-toluidine forms a stable complex with the silver salt, thus preventing ammine formation.

A single packing was tested; it contained a solution of concentration 394 μmole cm^{-3} and had $s = 0.0300\ cm^3\ g^{-1}$. The column was 92.9 cm long and contained 563 μmole silver nitrate at a linear concentration of 6.06 μmole cm^{-1}. Originally the packing was white, but it slowly turned brown over the course of weeks.

4.12.1 The chromatograms

The chromatogram is an asymmetrical peak with a steep front and a rear slope that approaches the base-line without prolonged tailing (Fig. 33). If the slight tail is eliminated by producing the rear slope to intersect the base-line, the point of intersection determines a final retention time (t_f in Expt. 13, Fig. 33) that proves to be independent of sample size. These results are very similar to those reported for the chromatography of aromatic vapours on an organo-clay derivative[37].

4.12.2 Numerical results

In Table 30 are listed the experimental conditions, values of the calibration factor (C), and V_c corresponding to t_f. The age of the packing is also given, because there is some indication that V_c slowly diminishes with time, an effect that may be related to the slow darkening of the packing.

At ages of not greater than 7 days, V_c was determined at 16.3 to 17.8°C and has an average and standard deviation of $3.85 \times 10^6\ cm^3\ mole^{-1}$ and $0.06 \times 10^6\ cm^3\ mole^{-1}$. In 4.14.4, p. 115, the values of C in Table 30 are used, together with those obtained with packings containing silver nitrate in mixtures of m-toluidine and benzonitrile, to determine an average value.

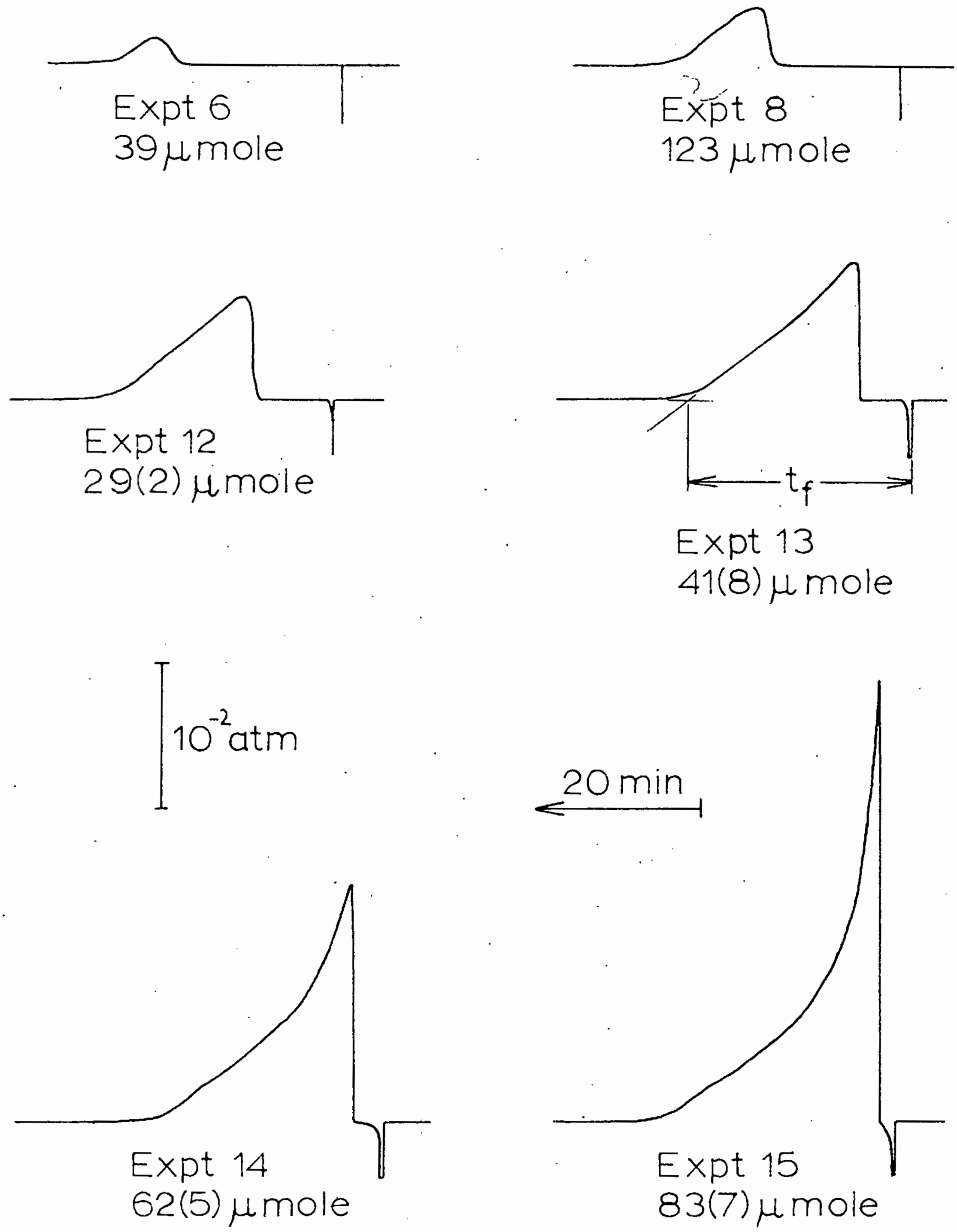


Figure 33. Silver nitrate in m-toluidine — effect of sample size. Flow-rate 98.(1)-98.(8) $cm^3 min^{-1}$, column temp. 16.7-17.7°C, packing age 7 days.

Table 30 Silver nitrate in m-toluidine - experimental conditions and results

Expt. no.	Flow-rate $cm^3\ min^{-1}$	Sample µmole	Column temp. deg C	10^3 C atm cm^{-1}	10^{-6} V_C $cm^3\ mole^{-1}$	Age days
1	9.8(1)	33(7)	17.5	2.29	3.27	73
2	9.9(0)	42(1)	17.7	2.31	3.31	73
3	34.6	28(9)	16.8	2.28	3.90	1
4	34.6	28(9)	16.8	2.20	3.78	1
5	34.5	124(3)	17.8	2.51	3.92	1
6	98.(2)	39	16.7	2.1(1)	3.89	7
7	98.(1)	81	16.9	2.0(8)	3.85	7
8	98.(5)	123	17.0	2.2(3)	3.80	7
9	98.(2)	124	16.3	2.0(7)	4.01	7
10	98.(1)	165	17.2	2.2(4)	3.82	7
11	98.(1)	208	17.1	2.23	3.84	7
12	98.(5)	29(2)	17.3	2.21	3.82	7
13	98.(1)	41(8)	17.7	2.30	3.79	7
14	98.(8)	62(5)	17.5	2.23	3.82	7
15	98.(5)	83(7)	17.4	2.36	3.82	7
16	98.(0)	166(8)	17.3	-	3.47	31

4.13 Silver perchlorate in m-toluidine

A packing containing silver perchlorate in m-toluidine behaves very similarly to one containing silver nitrate in the same solvent, but gives a higher value of V_c for the end of the chromatogram. Also, the detector response does not fall to the original base-line, but becomes steady at a new and higher base-line. The cause of this offset is not known; it occurs in every chromatogram, even when the experiments are made in quick succession, and can therefore not be a low and incompletely eluted plateau due to an ammine, since such a plateau would cause an apparent offset only after the first chromatogram. Furthermore, the offset increases considerably with increase in sample size, an effect not shown by a plateau due to an ammine.

A single packing was tested; it contained a solution of concentration 391 µmole cm^{-3} and had s = 0.0300 $cm^3\ g^{-1}$. The column was 92.3 cm long and contained 559 µmole of silver perchlorate at a linear concentration of 6.06 µmole cm^{-1}. The packing was used on the day of its preparation and was white.

In Table 31 the experimental conditions and results are reported; no values of C are given, because the offset makes it

Table 31 Silver perchlorate in m-toluidine - experimental conditions and results

Expt. no.	Flow-rate $cm^3\ min^{-1}$	Sample μmole	Column temp. deg C	$10^{-6}\ V_c^*$ $cm^3\ mole^{-1}$	Offset mm
1	99.(0)	122	17.4	4.58	2.3
2	99.(0)	122	17.4	4.51	2.3
3	97.(7)	28(9)	17.6	4.39	3.2
4	98.(6)	29(0)	17.2	4.35	3.1
5	98.(6)	62(2)	17.6	4.73	6.0

* Calculated from intersection of rear slope and final base-line.

impossible to determine the chromatogram area. V_c was determined at 17.2 to 17.6°C and has an average and standard deviation of $4.51 \times 10^6\ cm^3\ mole^{-1}$ and $0.15 \times 10^6\ cm^3\ mole^{-1}$.

4.14 Silver nitrate in benzonitrile and m-toluidine

Benzonitrile and m-toluidine are miscible in all proportions and packings containing silver nitrate in mixtures of these liquids show a gradual transition in chromatographic behaviour as the composition of the solvent is varied. An increase in the mole fraction of m-toluidine is accompanied by an increase in the dissociation pressure of the ammine responsible for the initial absorption by silver nitrate in benzonitrile, until at 28 mole% m-toluidine this pressure is high enough to produce a long, low plateau in the chromatogram and initial absorption is absent. Further increase in the mole fraction of m-toluidine causes the plateau to become higher, shorter and more sloping, until it is transformed at about 70 mole% m-toluidine into an asymmetrical peak similar to that produced by silver nitrate in m-toluidine. The plateau given by silver nitrate in benzonitrile persists unchanged in height to about 60 mole% m-toluidine, beyond which the chromatograms are too low to reach this plateau.

4.14.1 The packings

In Table 32 are listed the characteristics of the packings used, the solvent composition being given in column 2; for all packings s = 0.0300 cm^3 g^{-1}.

Table 32 Packings containing silver nitrate in benzonitrile and m-toluidine

Packing	Mole % m-toluidine	Concentration μmole cm^{-3}
NX1	28.2	396
NX2	31.4	394
NX3	39.3	395
NX4	42.6	396
NX5	48.6	358
NX6	48.6	395
NX7	61.3	395
NX8	73.9	394

The packings containing less than 50 mole% m-toluidine turned dark grey soon after preparation and before injection of ammonia; those richer in m-toluidine were white initially, but turned light brown over the course of weeks.

4.14.2 The chromatograms

The plateau marked III in Fig. 34 is the one resulting from increase in the dissociation pressure of the ammine responsible for initial absorption by silver nitrate in benzonitrile, and the changes in its length and height with changing solvent composition are obvious in the series of chromatograms shown. The shoulder marked II may perhaps be a plateau due to an ammine, but is so vestigial that its nature is doubtful. With the unattenuated bridge output used for the chromatograms in Fig. 34, the benzonitrile plateau (P_1) is off-scale; it is very short because of the high flow-rate. Fig. 35 shows the metamorphosis of plateau III into the m-toluidine peak. The effect of sample

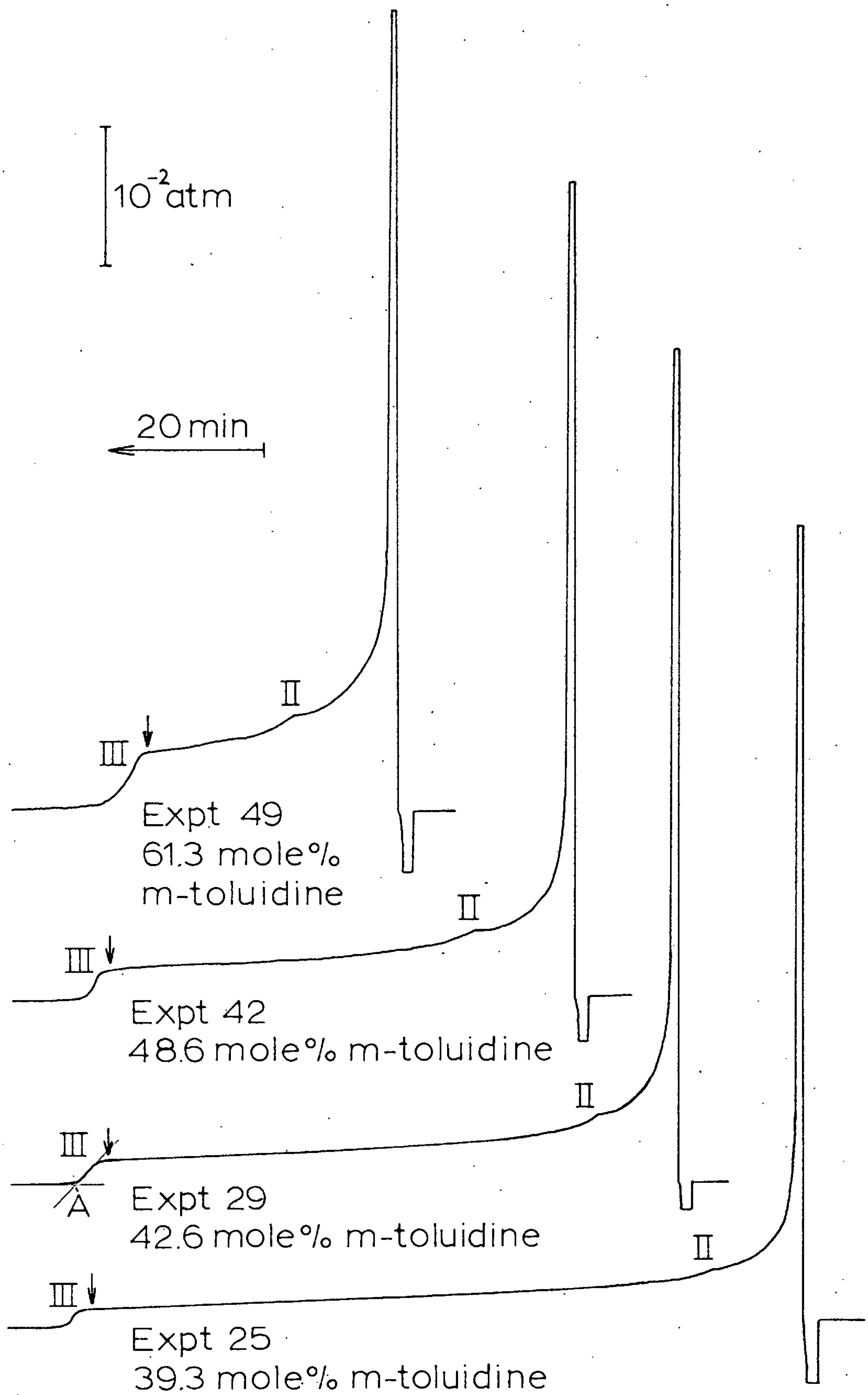


Figure 34. Silver nitrate in benzonitrile and m-toluidine—effect of solvent composition. Column length 90.6-93.4 cm, flow-rate 98.(0)-99.(2) $cm^3 min^{-1}$, sample size 124(1)-125(8) μmole, column temp. 17.0-17.9°C.

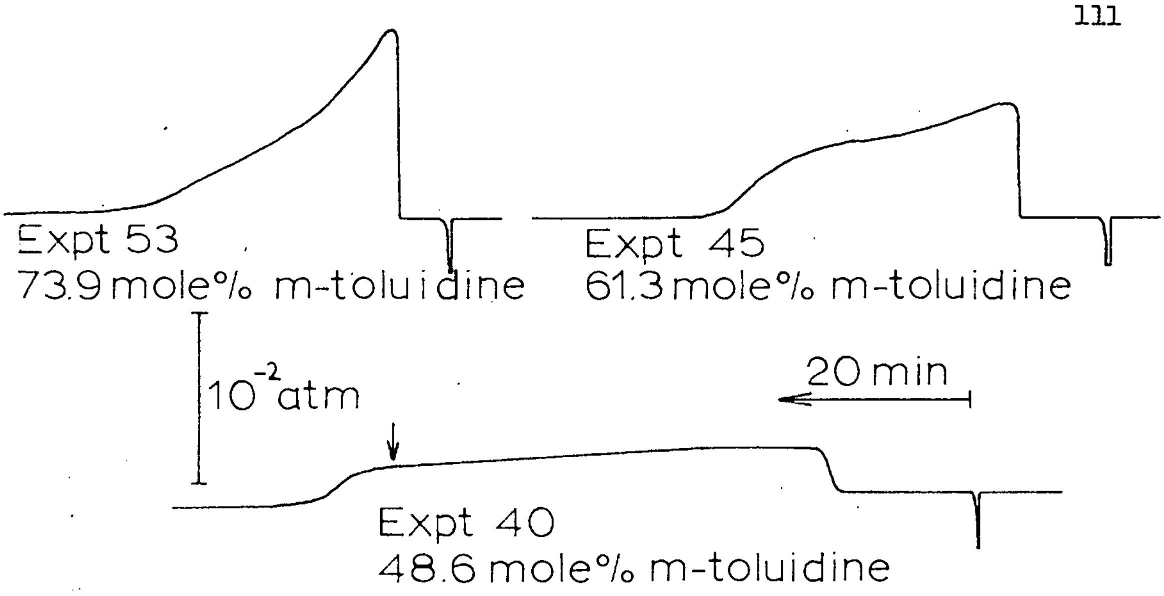


Figure 35. Silver nitrate in benzonitrile and m-toluidine—effect of solvent composition. Column length 83.9-91.3 cm, flow-rate 98.(0)-99.(2) $cm^3 min^{-1}$, sample size 55(1)-55(9) μmole, column temp. 17.0-17.8°C.

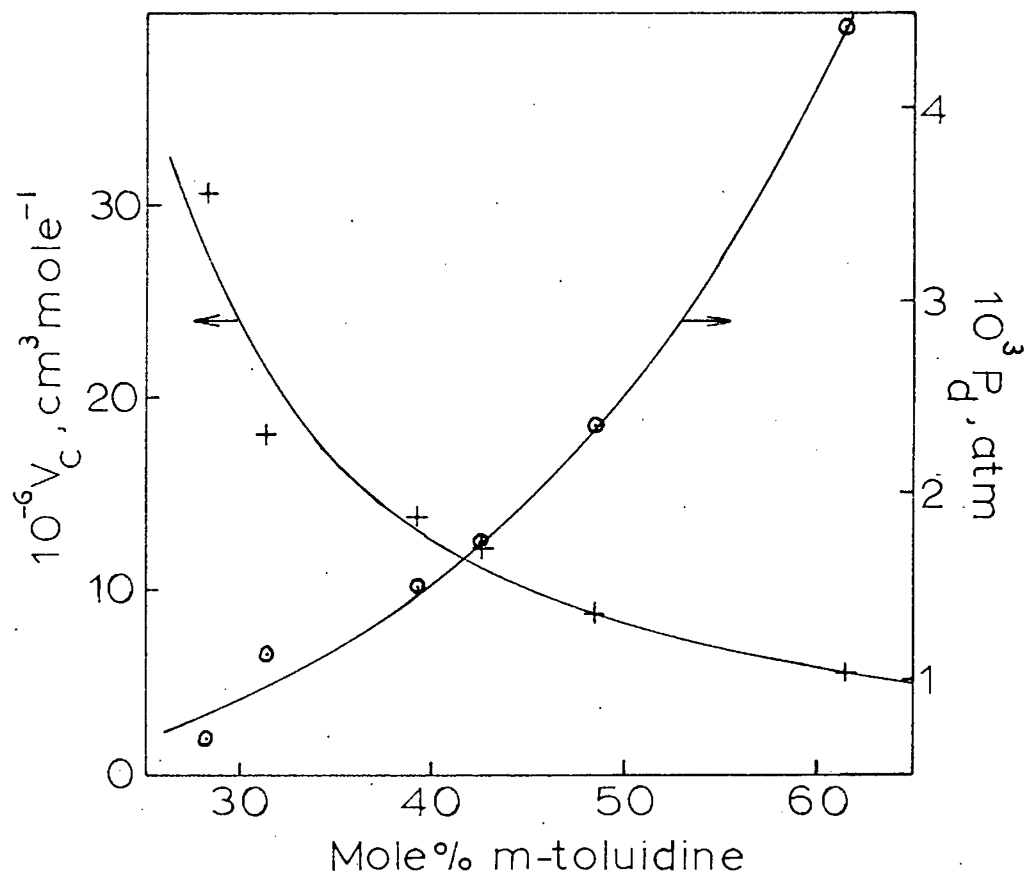


Figure 36. Silver nitrate in benzonitrile and m-toluidine—influence of solvent composition on lowest plateau.

size may be seen by comparing Expt. 42, Fig. 34, with Expt. 40, Fig. 35 and Expt. 49, Fig. 34 with Expt. 45, Fig. 35.

4.14.3 Numerical results

In Table 33 are listed the experimental conditions, measurements on plateau III and values of the calibration factor.

Table 33 Silver nitrate in benzonitrile and m-toluidine - experimental conditions and results

Expt. no.	Flow-rate $cm^3\ min^{-1}$	Sample μmole	Column temp. deg C	$10^3\ P_d$ atm	$10^{-6}\ V_c$ $cm^3\ mole^{-1}$	y	$10^3\ C$ atm cm^{-1}
Packing NX1, 28.2 mole% m-toluidine, 89.6 cm, 565 μmole silver nitrate, 6.31 μmole cm^{-1}							
17	98.(1)	105(3)	17.0	0.6(3)	28.7	0.76	-
18	98.(1)	162(0)	16.9	0.7(4)	32.5	1.01	-
Packing NX2, 31.4 mole% m-toluidine, 86.3 cm, 565 μmole silver nitrate, 6.55 μmole cm^{-1}							
19	98.(1)	41(9)	17.1	0.8(9)	18.6(6)	0.70	2.43
20	98.(2)	63(0)	17.0	1.0(9)	18.7(0)	0.86	2.19
21	98.(0)	104(3)	17.6	-	-	-	-
22	98.(1)	167(3)	17.2	1.4(5)	16.5(9)	1.01	-
Packing NX3, 39.3 mole% toluidine, 91.4 cm, 563 μmole silver nitrate, 6.16 μmole cm^{-1}							
23	98.(0)	49(8)	17.3	1.7(6)	13.7(3)	1.01	2.53
24	98.(0)	83(3)	17.3	1.3(4)	14.2(8)	0.80	2.27
25	98.(0)	125(1)	17.4	1.4(9)	13.3(3)	0.83	-
26	97.(8)	166(9)	17.3	1.4(1)	13.7(7)	0.81	-
Packing NX4, 42.6 mole% m-toluidine, 91.8 cm, 567 μmole silver nitrate, 6.18 μmole cm^{-1}							
27	98.(8)	41(2)	18.0	1.8(5)	12.2(7)	0.95	2.43
28	98.(0)	82(7)	17.6	1.6(1)	12.7(8)	0.86	2.29
29	98.(1)	125(0)	17.9	1.7(2)	11.2(5)	0.81	-
30	98.(0)	166(6)	17.3	-	-	-	-
Packing NX5, 48.6 mole% m-toluidine, 71.2 cm, 398 μmole silver nitrate, 5.59 μmole cm^{-1}							
31	114.(3)	29(1)	17.7	2.5(9)	8.47	0.92	2.10
32	114.(3)	37(6)	17.7	2.4(1)	8.77	0.89	2.20
Packing NX5, 48.6 mole% m-toluidine, 93.4 cm, 513 μmole silver nitrate, 5.49 μmole cm^{-1}							
33	33.9	124(9)	17.8	-	-	-	-
34	117.(7)	41(7)	17.2	2.2(8)	8.40	0.80	2.22
35	117.(7)	62(3)	17.2	2.3(9)	7.73	0.77	2.23
36	117.(7)	83(7)	17.2	2.3(5)	7.73	0.76	2.24
37	121.(1)	125(7)	17.3	2.3(7)	7.51	0.75	-

Table 33 (continued)

Expt. no.	Flow-rate cm^3 min^{-1}	Sample μmole	Column temp. deg C	10^3 P_d atm	10^{-6} V_c cm^3 $mole^{-1}$	y	10^3 C atm cm^{-1}
Packing NX6, 48.6 mole% m-toluidine, 91.3 cm, 557 μmole silver nitrate, 6.11 μmole cm^{-1}							
38	98.(9)	207	18.1	2.2(2)	8.38	0.78	2.29
39	99.(0)	33(3)	18.3	2.2(8)	8.67	0.83	2.13
40	99.(2)	55(1)	17.0	2.2(3)	9.94	0.93	2.22
41	99.(2)	55(1)	17.0	2.3(0)	9.53	0.92	2.15
42	99.(2)	125(8)	17.0	2.2(3)	8.99	0.84	-
Packing NX7, 61.3 mole% m-toluidine, 90.6 cm, 565 μmole silver nitrate, 6.23 μmole cm^{-1}							
43	98.(6)	38	17.7	-	5.69	-	3.0(5)
44	98.(6)	205	17.8	-	5.72	-	2.24
45	98.(0)	55(7)	17.8	-	5.90	-	2.24
46	98.(0)	55(7)	17.8	-	5.75	-	2.22
47	98.(8)	104(3)	17.5	4.5(7)	4.73	0.91	-
48	98.(0)	124(1)	17.8	4.1(9)	5.23	0.92	-
49	98.(0)	124(1)	17.8	4.2(2)	5.28	0.93	-
50	97.(9)	166(7)	17.7	4.6(4)	4.58	0.89	-
Packing NX8, 73.9 mole% m-toluidine, 83.9 cm, 565 μmole silver nitrate, 6.73 μmole cm^{-1}							
51	97.(8)	38	18.3	-	4.62	-	2.5(2)
52	98.(6)	205	18.0	-	4.58	-	2.26
53	98.(0)	55(9)	17.7	-	4.77	-	2.23
54	98.(6)	56(0)	17.6	-	4.74	-	2.22
55	97.(8)	82(6)	18.0	-	4.65	-	-
56	97.(0)	166(7)	17.4	-	4.47	-	-

The numbers of the experiments continue the sequence started in Table 30, p.107, because results in both tables are used in 4.14.4. Plateau III slopes over its whole length, and P_d is measured near the rear end, as indicated by arrows in Figs. 34 and 35. The final retention volume, corresponding to point A in Fig. 34, Expt. 29, is used to calculate V_c, because this volume can be found for chromatograms like Fig. 35, Expts. 53 and 45, that have no plateau, and values of V_c thus found can be compared for the whole range of solvent composition. No better choice than point A is available for the rear end, because the sloping of the plateau makes it impossible to reconstruct the ideal, undecayed plateau.

The values of y suggest the composition $AgX.NH_3$ for the lowest ammine, whereas $AgX(NH_3)_{1.5}$ or $AgX(NH_3)_2$ is postulated for the initially absorbing ammine of silver nitrate in benzonitrile (see 4.6.8, p.76). Perhaps the latter system absorbs ammonia in two stages,

$$AgX + NH_3 \rightleftharpoons AgX.NH_3$$

$$\text{and } AgX.NH_3 + 0.5NH_3 \rightleftharpoons AgX(NH_3)_{1.5}$$

$$\text{or } AgX.NH_3 + NH_3 \rightleftharpoons AgX(NH_3)_2 ,$$

and the second of these stages produces the vestigial plateau II when m-toluidine is present. It is also possible that part of the initial absorption is prevented even at very low concentrations of m-toluidine and the remaining part corresponds to y in Table 33.

The increase in P_d and decrease in V_c with increasing mole fraction of m-toluidine are clearly evident in Table 33; the averages of these quantities for each solvent composition are collected in Table 34 and plotted in Fig. 36. The relationship

Table 34 Silver nitrate in benzonitrile and m-toluidine - average results for lowest plateau

Mole% m-toluidine	Temp. deg C	10^3 P_d atm	10^{-6} V_c cm^3 $mole^{-1}$
28.2	16.9 - 17.0	0.69	30.6
31.4	17.0 - 17.6	1.14	17.98
39.3	17.3 - 17.4	1.50	13.78
42.6	17.2 - 18.0	1.73	12.10
48.6	17.0 - 18.3	2.33	8.47
61.3	17.5 - 17.8	4.41	5.36
73.9	17.4 - 18.3	-	4.64

between P_d and solvent composition shows that m-toluidine loosens the salt-ammonia bond in the ammine (or one of the ammines) responsible for initial absorption by silver nitrate in benzonitrile, while the constancy of y shows that the ammonia content of this ammine is not affected by m-toluidine.

In Table 35 measurements on the vestigial plateau II and the benzonitrile plateau (called plateau I) are recorded. The values of V_c and y for plateau I are very rough, because the

Table 35 Silver nitrate in benzonitrile and m-toluidine - measurements on the two higher plateaux

Expt. no.	Mole% m-toluidine	10^3 Pd atm		10^{-6} V_c cm^3 $mole^{-1}$		y	
		Plat I	Plat II	Plat I	Plat II	Plat I	Plat II
17	28.2	-	2.9(9)	-	1.4(5)	-	0.18
18	"	-	2.5(0)	-	1.3(5)	-	0.14
21	31.4	-	4.0(2)	-	1.4(7)	-	0.25
22	"	77.(6)	-	0.3(2)	-	1.0	-
25	39.3	-	4.0(2)	-	1.5(0)	-	0.25
26	"	75.(9)	-	0.2(4)	-	0.7	-
29	42.6	-	5.0(7)	-	1.5(1)	-	0.32
30	"	77.(7)	-	0.2(7)	-	0.9	-
33	48.6	75.(0)	-	0.2(9)	-	0.9	-
36	"	-	4.7(5)	-	2.0(9)	-	0.42
37	"	76.(3)	5.2(7)	0.2(6)	2.0(5)	0.8	0.44
42	"	-	4.8(8)	-	1.8(5)	-	0.38
46	61.3	-	7.2(3)	-	1.9(6)	-	0.59
47	"	-	7.1(4)	-	1.9(8)	-	0.59
50	"	79.(6)	-	0.2(7)	-	0.9	-

retention time is very short at the high flow-rates used and the starting time of the experiments is indefinite, owing to the injection of the large samples in three or four portions. V_c for plateau II is calculated from the retention time of the shoulder.

For plateau I, P_d and V_c are independent of the solvent composition, while for plateau II both these quantities increase with increasing mole fraction of m-toluidine. P_d and V_c should vary in opposite directions, as for plateau III, and the values of V_c for plateau II are therefore of doubtful significance.

The slope of plateau III makes it unsuitable for treatment by Method 1.

4.14.4 The calibration factor

All the values of C in Tables 30 and 33 are collected in Table 36, together with values of the carrier flow-rate, column temperature and maximum chromatogram height. The values marked

Table 36 The detector calibration factor

Expt. no.	Flow-rate $cm^3\ min^{-1}$	Column temp. deg C	Maximum height cm	10^3 C atm cm^{-1}
1	9.8(1)	17.5	4.89	2.29
2	9.9(0)	17.7	6.27	2.31
3	34.6	16.8	3.70	2.28
4	34.6	16.8	3.90	2.20
5	34.5	17.8	54.5	2.51*
19	98.(1)	17.1	0.49	2.43*
43	98.(6)	17.7	0.60	3.0(5)*
51	97.(8)	18.3	0.61	2.5(2)*
20	98.(2)	17.0	0.78	2.1(9)*
23	98.(0)	17.3	0.79	2.5(3)*
6	98.(2)	16.7	0.80	2.1(1)*
27	98.(8)	18.0	0.83	2.43*
38	98.(9)	18.1	0.95	2.29
39	99.(0)	18.3	1.18	2.13
40	99.(2)	17.0	1.30	2.22
41	99.(2)	17.0	1.38	2.15
7	98.(1)	16.9	1.45	2.0(8)
8	98.(5)	17.0	1.80	2.23
44	98.(6)	17.8	1.81	2.24
9	98.(2)	16.3	1.83	2.0(7)
24	98.(0)	17.3	2.02	2.27
28	98.(0)	17.6	2.06	2.29
52	98.(6)	18.0	2.20	2.26
10	98.(1)	17.2	2.20	2.2(4)
11	98.(1)	17.1	2.60	2.23
45	98.(0)	17.8	3.01	2.24
46	98.(0)	17.8	3.09	2.22
12	98.(5)	17.3	3.29	2.21
13	98.(1)	17.7	4.43	2.30
53	98.(0)	17.7	5.04	2.23
54	98.(6)	17.6	5.11	2.22
14	98.(8)	17.5	7.49	2.23
15	98.(5)	17.4	13.73	2.36
31	114.(3)	17.7	1.42	2.10
32	114.(3)	17.7	1.58	2.20
34	117.(7)	17.2	1.39	2.22
35	117.(7)	17.2	2.25	2.23
36	117.(7)	17.2	17.68	2.24

with asterisks are of low accuracy, because they are found from inaccurate chromatogram areas - in Expt. 5 the accuracy of area measurement is reduced by high bridge attenuation and for the other experiments the chromatograms are so low that a small error in locating the base-line introduces a large error in the area. The remaining 30 values were obtained under the following conditions :

flow-rate	9.8 - 118 $cm^3\ min^{-1}$
column temperature	16.8 - 18.3°C

maximum chromatogram height	0.95 - 17.68 cm
bridge current	150 ma

and have an average and standard deviation of 2.23×10^{-3} atm cm^{-1} and 0.07×10^{-3} atm cm^{-1}.

With this calibration factor, the lowest ammonia pressure that can be detected is about 0.4×10^{-3} atm.

4.15 Lead halides

Some early experiments were performed with packings of solid ammine-forming salts, and lead halides were selected for such packings because they are non-hygroscopic and therefore easily handled. The two halides used, bromide and chloride, were prepared for the columns as described in 3.3, p.35, and under certain conditions yielded ammonia chromatograms showing a peak and a plateau deformed by a valley.

4.15.1 Lead bromide

The single packing used was a screen fraction of 16-36 mesh and occupied a length of 92.6 cm in the column; it was not weighed, but its weight is estimated to be 50-60 g.

At room temperature, an 89 μmole sample of ammonia did not emerge at all, while at 179° C, the chromatograms were tailing peaks with low retention times. In experiments at 86° to 125° C, the chromatograms consisted of a peak followed by a plateau, as shown in Figs. 37-39. The scales of ordinates in these figures are given in cm instead of atm because the katharometer response depends on temperature and the calibration factor is known for room temperature only.

It is evident from the figures that sample size affects the chromatograms in the way predicted in 2.3.1, p.13, for a complex-forming fixed phase. The ammonia samples are of the order of 10^2 μmole, while the packing contains more than 10^5 μmole of lead bromide - this proves that the reaction between the ammonia

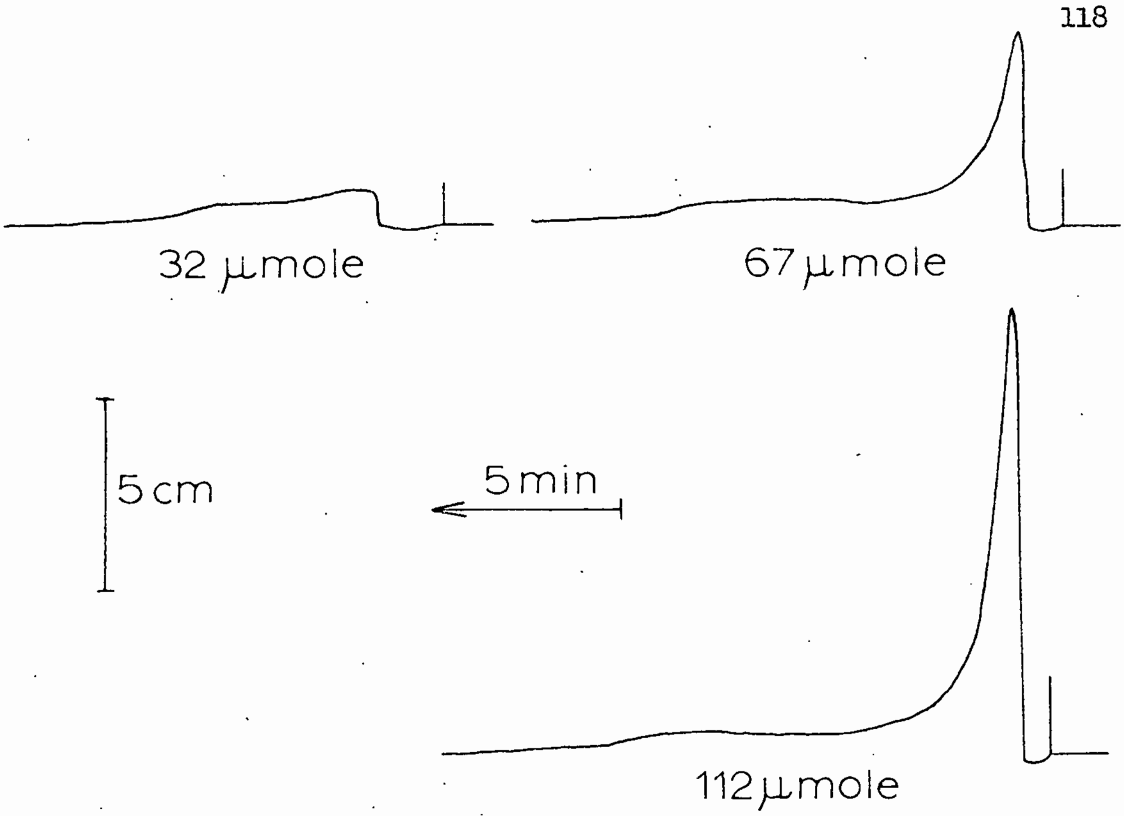


Figure 37. Lead bromide—effect of sample size. Flow-rate 121-123 $cm^3 min^{-1}$, column temp. 86°C.

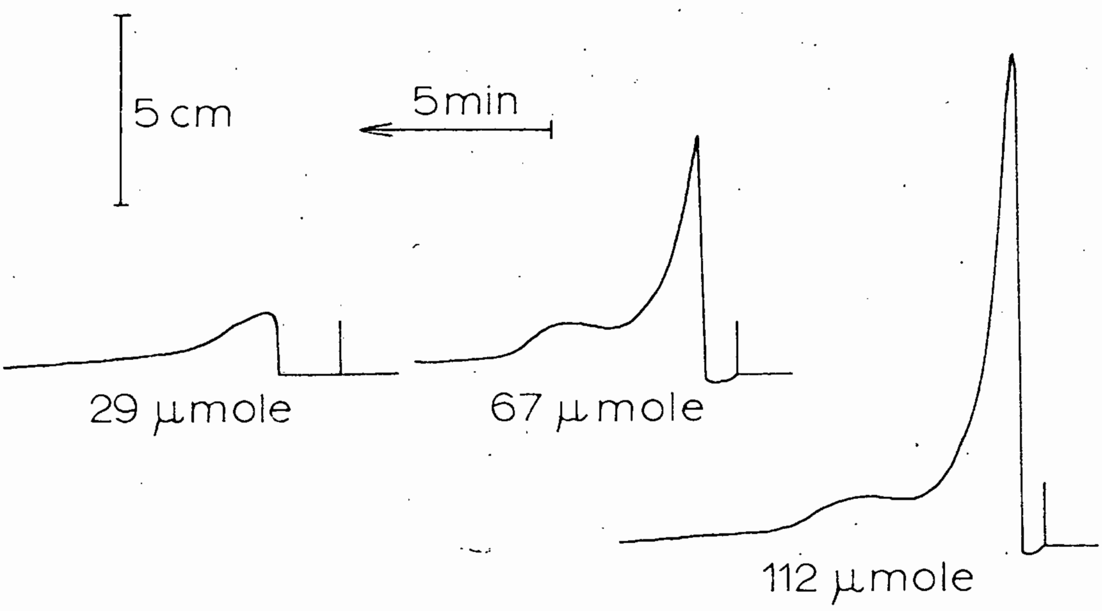


Figure 38. Lead bromide—effect of sample size. Flow-rate 125-130 $cm^3 min^{-1}$, column temp. 99°C.

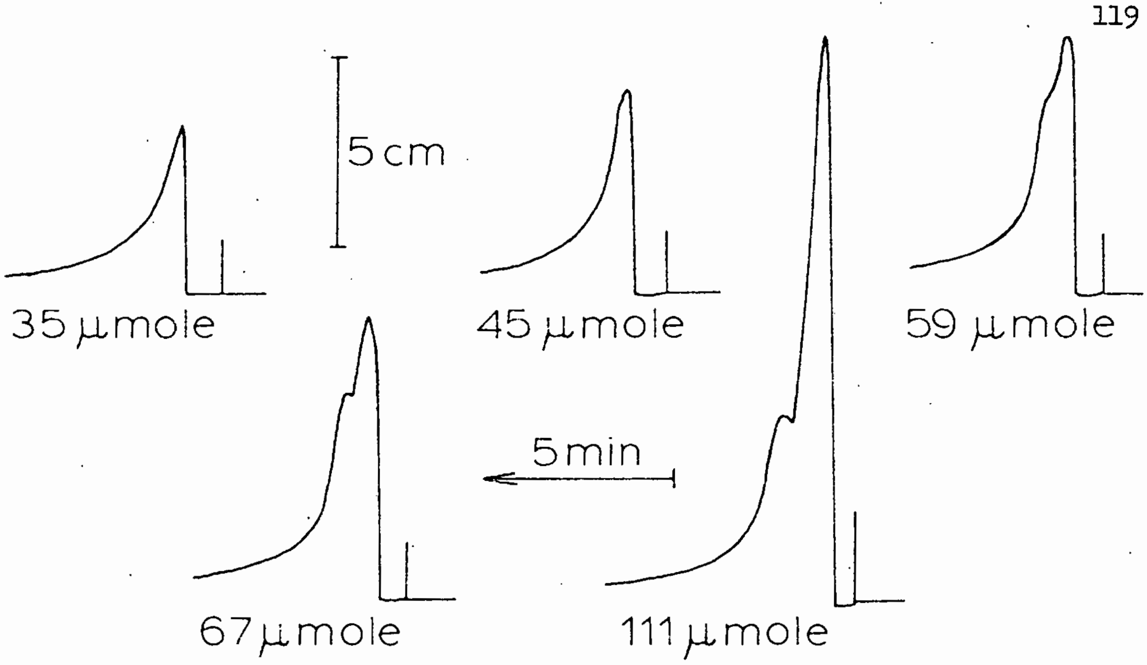


Figure 39. Lead bromide—effect of sample size. Flow-rate 136-139 $cm^3 min^{-1}$, column temp. 125°C.

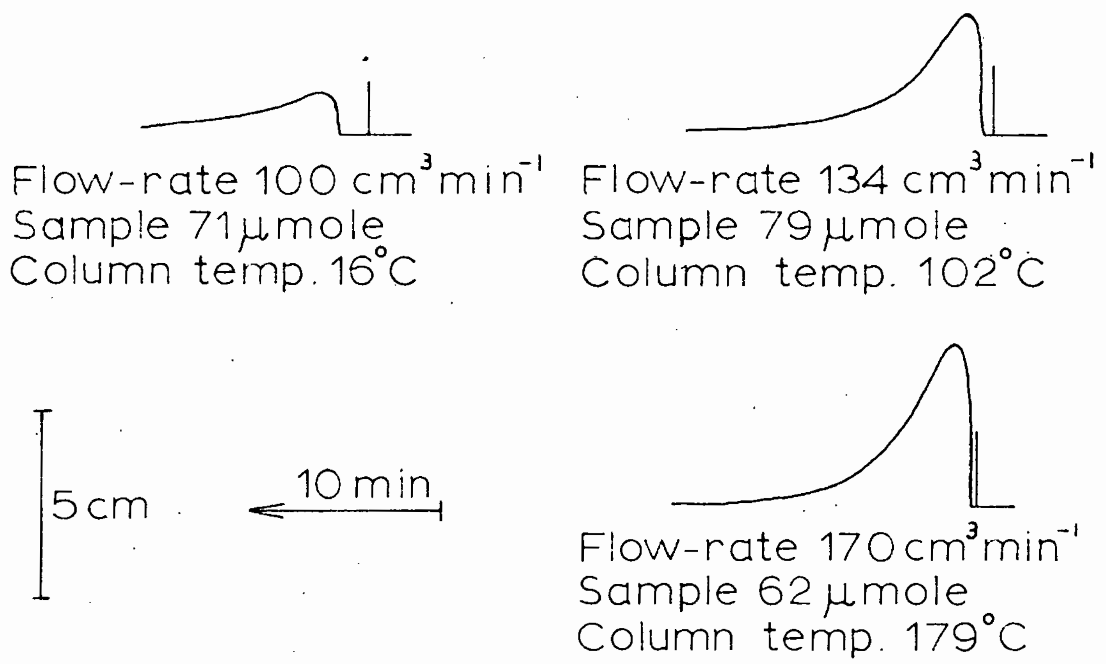


Figure 40. Lead chloride—chromatograms obtained with freshly prepared packing.

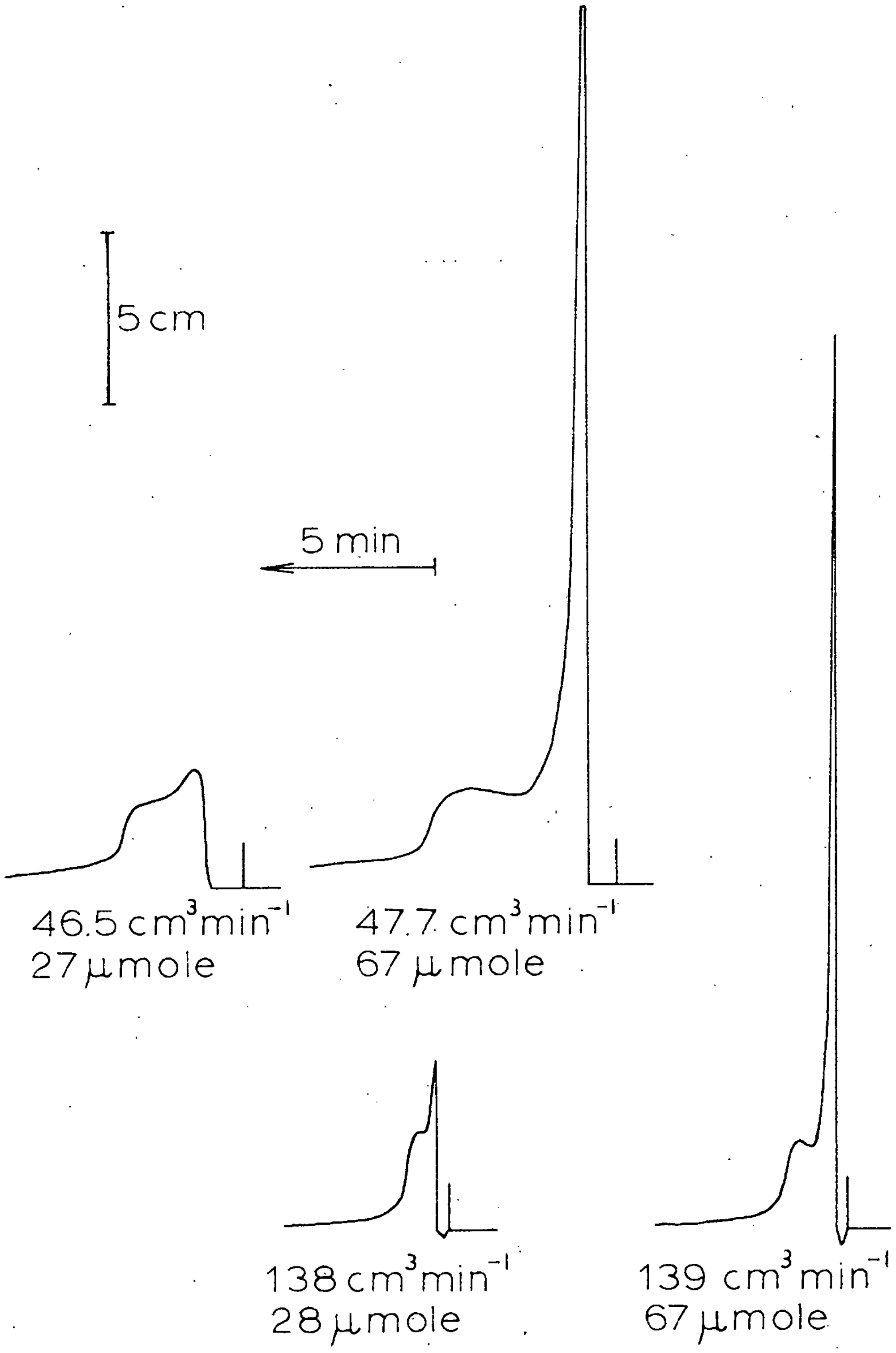


Figure 41. Lead chloride—effect of flow-rate and sample size. Column temp. 112°C.

and the salt is confined to the surface of the latter, otherwise no peak would precede the plateau.

4.15.2 Lead chloride

The single packing used was a screen fraction of 36-60 mesh, occupied 92.2 cm in the column and weighed 46.4 g.

Up to 2 days after its preparation, the packing gave chromatograms of the kind shown in Fig. 40. These are remarkable for the small influence of column temperature, which was varied from 16° to 179°C ; in most applications of gas-solid chromatography, a temperature variation of this magnitude causes a tremendous change in retention time. Chromatograms similar to those of Fig. 40 were also obtained at 70°, 124° and 154° C.

After being tested for 2 days, the packing was transferred to a stoppered bottle and stored for 39 days, after which it was repacked in the column. It now gave totally different chromatograms, which had a plateau in experiments at 79° to 146° C. Examples illustrating the influence of sample size and flow-rate are shown in Fig. 41; these factors act as predicted in 2.3.1, p.13, for a complex-forming fixed phase. As for lead bromide, the sample size and the amount of fixed phase differ by 3 orders of magnitude, and this shows that ammine formation takes place only on the surface of the lead chloride.

4.16 The effect of carrier humidity

It has been reported[38] that a rise in the temperature of a gas-chromatographic column causes the elution of moisture and other impurities taken up by the packing from the carrier at a lower temperature. In the present work, evidence has been obtained that such moisture can also be displaced by an ammonia sample from packings containing salts. Under certain conditions, the sample emerges to produce a chromatogram with two peaks or a peak preceded by a step, and the first peak or step is ascribed to displaced moisture, since its size increases with increasing humidity of the carrier gas.

Particulars of the packings and experimental conditions that gave such chromatograms are listed in Table 37. The soaps

Table 37 Packings showing moisture displacement

Fixed phase	Solid support	s mg g^{-1}	Column length cm	Packing weight g	Carrier gas	Column temp. deg C
Zinc dialkyldithiophosphate in mineral oil	Glass beads, 0.4 mm diam.	1.678	84.9	48.96	N_2	23, 79, 112.
Zinc oleate	Granular copper, 36-60 mesh	32.7	92.0	68.62	N_2	136, 139, 166, 171, 173, 178, 179, 180
					CO_2	173, 175
Copper oleate	Granular copper, 36-60 mesh	25.3	92.7	66.46	N_2	109, 140, 172
Nickel stearate	Granular copper, 36-60 mesh	28.6	92.6	68.12	N_2	163, 173
Anhydrous calcium chloride 16-36 mesh	-	-	91.3	-	N_2	109, 167, 177

were distributed over the solid support by means of a volatile solvent (carbon tetrachloride for zinc oleate, ethyl ether for copper oleate) or liquid forming a fine suspension (carbon tetrachloride for nickel stearate).

Figs. 42-44 show a selection of ammonia chromatograms having two peaks or a peak preceded by a step. Fig. 42(c) and (d) and Fig. 43 (b) and (c) show the effect of varying carrier humidity; chromatograms like Fig. 43 (b) and (c) were reproducible in alternation. The difference between Fig. 43 (d) and (e) is consistent with the view that the first peak is due to moisture in the carrier, because the low temperature of dry ice reduces the

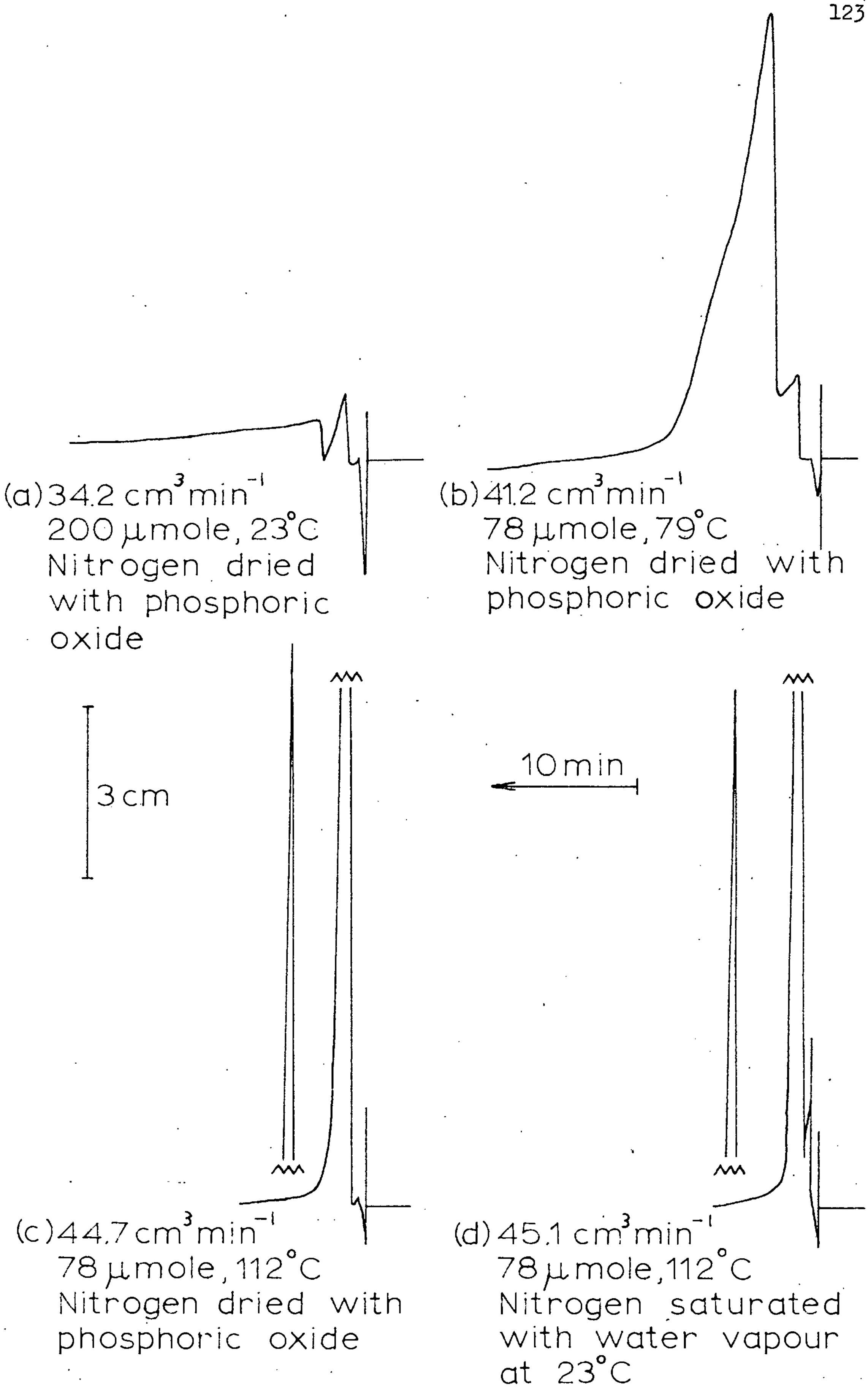


Figure 42. Zinc dialkyldithiophosphate in mineral oil—moisture displacement. Data with chromatograms are flow-rate, sample size, column temp. and carrier.

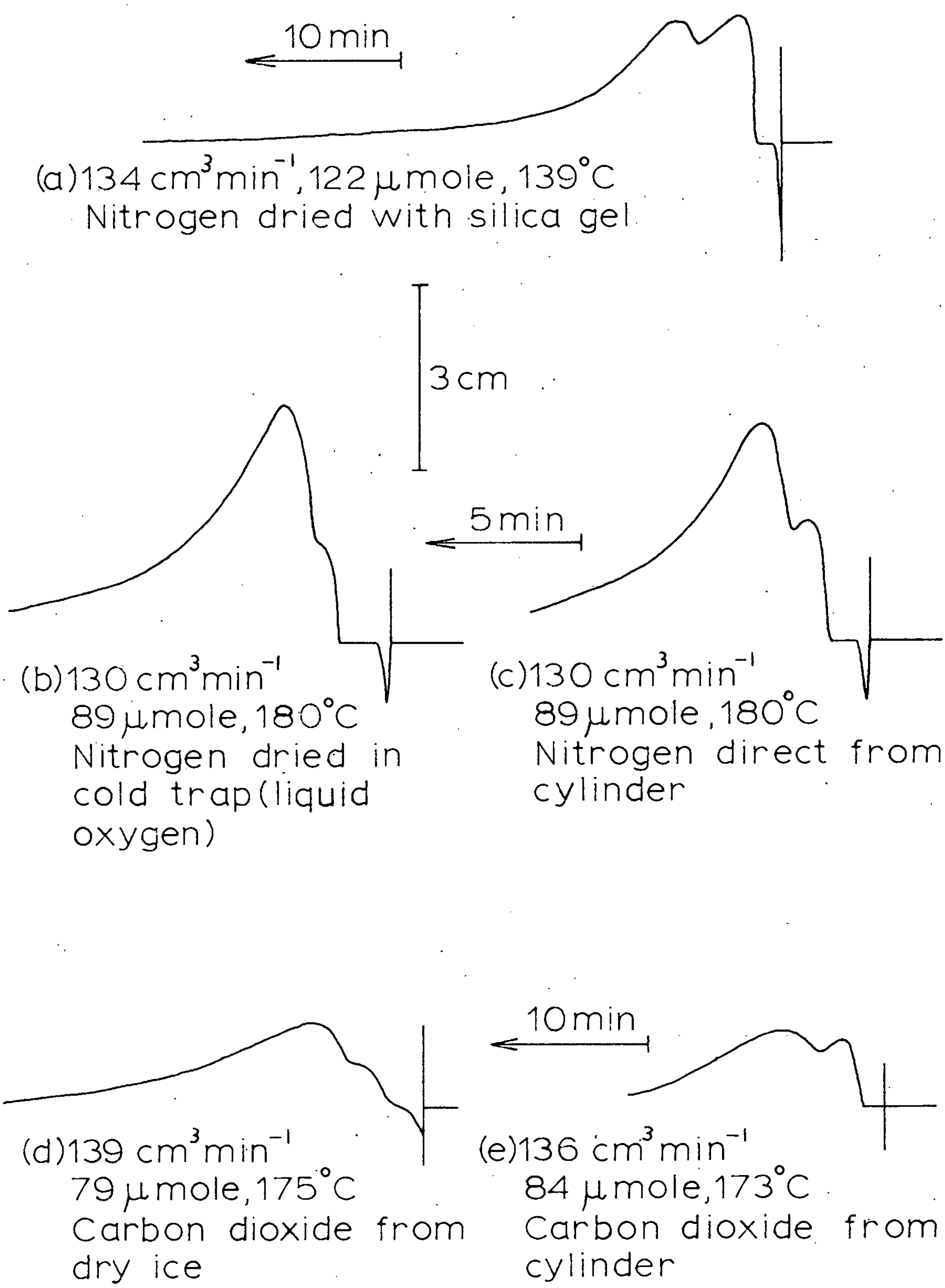
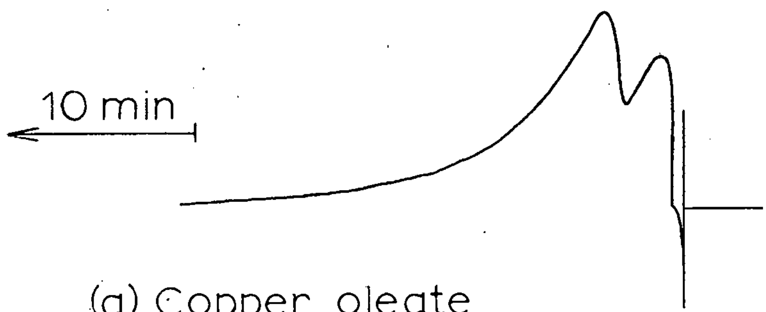
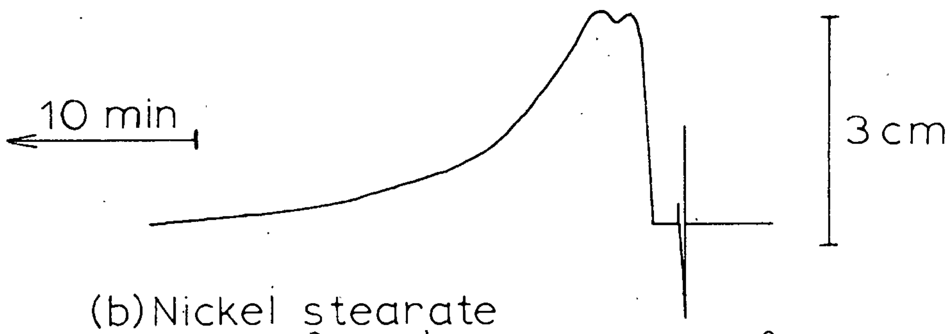


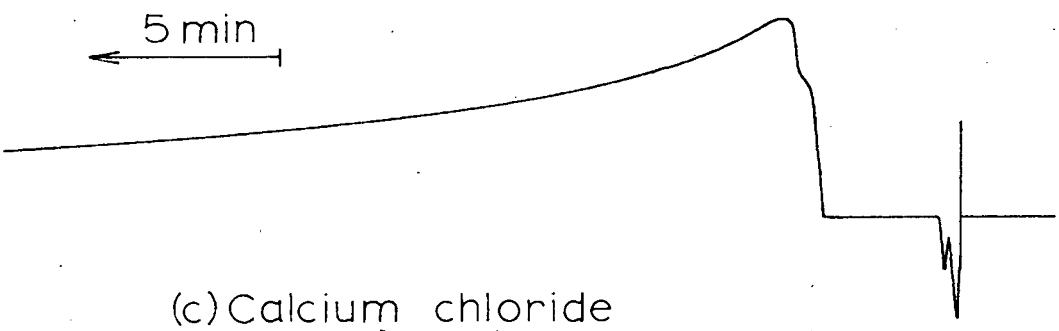
Figure 43. Zinc oleate—moisture displacement. Data with chromatograms are flow-rate, sample size, column temp. and carrier.



(a) Copper oleate
132 $cm^3 min^{-1}$, 117 μmole, 140°C
Nitrogen dried with silica gel



(b) Nickel stearate
146 $cm^3 min^{-1}$, 128 μmole, 163°C
Nitrogen dried with silica gel



(c) Calcium chloride
147 $cm^3 min^{-1}$, 68 μmole, 177°C
Nitrogen dried in cold trap
(liquid oxygen)

Figure 44. Copper oleate, nickel stearate and calcium chloride — moisture displacement. Data with chromatograms are flow-rate, sample size, column temp. and carrier.

vapour pressure of any moisture impurity. The fact that a step is present in Fig. 43 (b) and Fig. 44 (c), even though the carrier was passed through a cold trap, may be due to incomplete drying in the latter or recontamination with moisture in short rubber tubes connecting the sample injector to the column.

4.17 Charcoal

In the gas chromatography of ammonia on charcoal, it was found that this adsorbent gives extremely irreproducible results, even in a single series of experiments with the same column. Usually the chromatograms are the steep-fronted, tailing peaks typical of adsorbents, but sometimes a displacement step precedes the peak. A few examples of such steps are given here for comparison with the results reported in 4.16.

The packings were prepared by crushing charcoal blocks, screening to 36-60 mesh, washing with water to remove dust and drying for a few hours in an oven at about 200° C.

Fig. 45 (a) shows the most pronounced step observed; 5 days later the same column, which had meanwhile been stored stoppered at room temperature, gave the chromatograms of Fig. 45 (b) and (c). In these the step is much smaller and is unaffacted by the degree of desiccation of the carrier gas; this indicates that the step is not due to moisture taken up from the carrier, but no experiments were made with moister carrier gas to verify this conclusion. After being rewashed and dried, the packing gave the chromatograms of Fig. 45 (d) and (e) which have a long step, also unaffected by the degree of desiccation of the carrier. The chromatogram of Fig. 45 (f) was obtained after the packing had been raised to a dull red heat in a muffle furnace, cooled in a desiccator and repacked immediately.

If the displacement step is not due to moisture, it may be due to adsorbed oxygen, carbon monoxide or carbon dioxide.

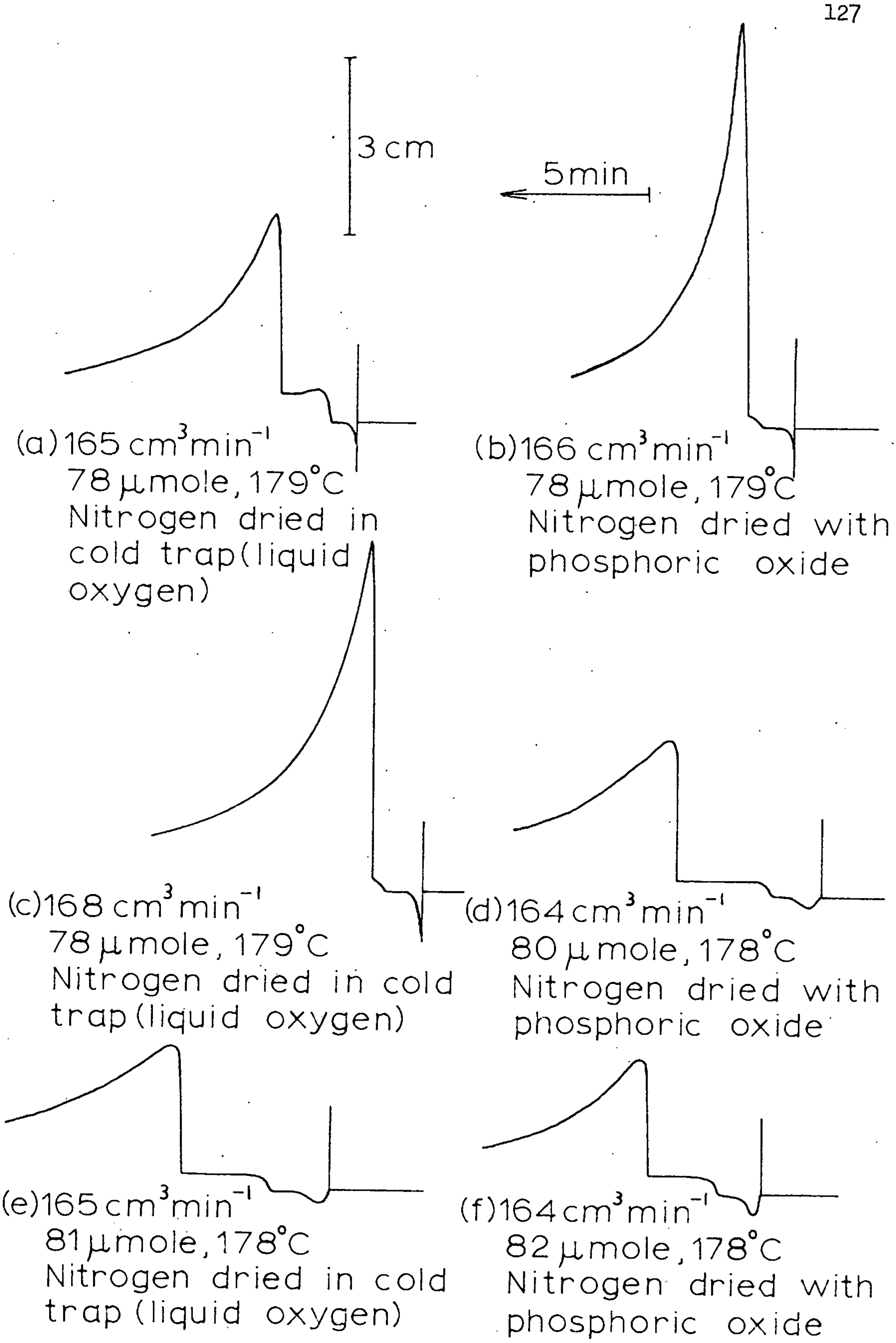


Figure 45. Charcoal—displacement step. Data with chromatograms are flow-rate, sample size, column temp. and carrier.

These results show that great care is necessary in preparing charcoal for the gas chromatography of ammonia.

SECTION 5

CONCLUSION

In this section, the results obtained for solutions of silver salts are correlated and the gas-chromatographic method of studying ammines is compared with other methods.

5.1 Correlation of results for solutions of silver salts

Because only a few salt-solvent systems have been studied and most of the numerical results are of low accuracy, only tentative and provisional correlations can be suggested.

Both the solvent and the anion affect ammine formation, the influence of the solvent being pronounced. This suggests that solid compounds precipitated by ammonia from some solutions contain the solvent as well as ammonia. The nitrogen atoms in benzonitrile and benzyl cyanide and the oxygen atom in fenchone may form dative bonds with silver ions; in addition, these substances, as well as tetralin, may be structurally bound in the crystal. A complete investigation of ammine composition would require not only the determination of ammonia content, but also the estimation of any bound solvent. m-Toluidine prevents ammine formation by itself forming with the silver ion a stable complex that remains in solution.

Fig. 46 is a logarithmic plot of all the dissociation pressures obtained, each pressure being shown as the range defined by its standard deviation (for fenchone the actual range of pressures for the P_2 plateau is shown). The salt-solvent systems are designated according to the code used for packings, explained in 4.1, p.40. The figures near the bottom of the diagram are experimental values of the initial absorption (moles of ammonia per mole of salt), while those higher up are ammine compositions (moles of ammonia per mole of salt, excess over next lower ammine) suggested by values of y. It is evident that the

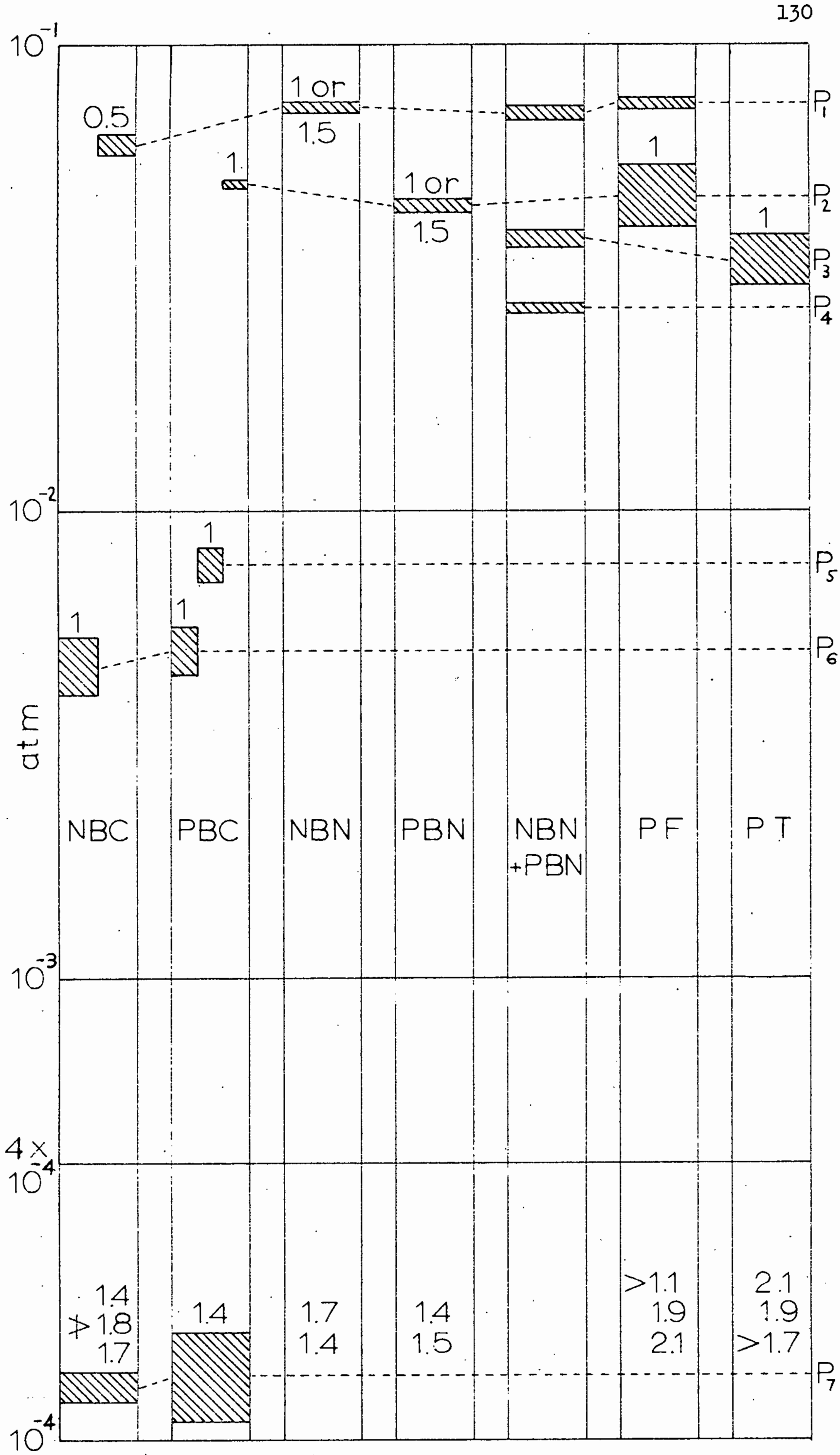


Figure 46. Correlation of results for solutions of silver salts.

pressures fall into three groups : those below 0.4×10^{-3} atm, a small group between 4.0×10^{-3} and 8.3×10^{-3} atm, and a large group between 26×10^{-3} and 77×10^{-3} atm. It appears that certain values of the dissociation pressure are shown by more than one system, as indicated by the broken lines linking pressure ranges. These recurring pressures, as well as the isolated values, have been designated throughout this thesis by the symbols on the right of Fig. 46. Table 38 shows averages, followed by standard deviations, of P_1, P_2 (excluding P_2 for silver perchlorate in fenchone), P_3, P_6' and P_7, the values being pressures in atm, multiplied by 10^3; column 9 shows the overall averages and standard

Table 38 Correlated dissociation pressures

	NBC	PBC	NBN	PBN	NBN+PBN	PF	PT	Overall
P_1	67.6 3.5	- -	73.0 2.0	- -	71.2 2.8	74.9 2.3	- -	71.3 3.7
P_2	- -	50.4 1.2	- -	48.1 1.7	- -	- -	- -	48.5 1.8
P_3	- -	- -	- -	- -	38.2 1.6	- -	35.2 3.9	35.8 3.8
P_6	4.66 0.66	5.01 0.60	- -	- -	- -	- -	- -	4.73 0.67
P_7	0.13 0.01	0.14 0.03	< 0.4 -	<0.4 -	< 0.4 -	< 0.4 -	< 0.4 -	0.13 0.04

deviations for all the contributing systems. The overall standard deviations are nearly equal to the largest standard deviations for individual systems, and this is some justification for the suggested correlations.

There is some indication that for the formation of the lowest two ammines, the following equations are common :

$$AgX + 2NH_3 \rightleftharpoons AgX(NH_3)_2 \quad \text{.........................} \quad (i)$$

$$AgX(NH_3)_2 + NH_3 \rightleftharpoons AgX(NH_3)_3 \ . \quad \text{.........................} \quad (ii)$$

These equations have been postulated in Section 4 for the systems PF and PT, the equilibrium pressures for equation (ii) being P_2

and P_3 respectively. For NBN and PBN, equation (i) holds if there is about 30% decomposition of the salt in the column, but then the ammonia coefficient of unity in equation (ii) is too low. If the initial absorption by NBC is supplemented by further, unobserved absorption during ageing, then the equations may also be valid for this system, the equilibrium pressure for reaction (ii) being P_6. For a fresh PBC packing, P_7 and P_5 are the lowest two pressures; the P_6 ammine decomposes to give one ammonia molecule per silver atom, in accordance with equation (ii), but the initial absorption is too low for equation (i); for an older packing, P_6 follows P_7 and also decomposes to give one ammonia molecule per silver atom.

That the anion affects ammine formation, may be seen by comparing the results for silver nitrate and silver perchlorate in benzyl cyanide and benzonitrile. In both these solvents, silver nitrate forms P_1 ammines and silver perchlorate forms P_2 ammines. Although both salts form P_6 ammines in benzyl cyanide, only silver perchlorate forms a P_5 ammine. When silver nitrate and silver perchlorate are present together in benzonitrile, the P_1 ammine of silver nitrate persists, but the P_2 ammine of silver perchlorate is replaced by P_3 and P_4 ammines.

Although benzonitrile and benzyl cyanide are adjacent members of a homologous series, there are pronounced differences between the solutions in these liquids. The solutions in benzyl cyanide change on ageing, whereas those in benzonitrile do not (except the mixed packing containing both nitrate and perchlorate), and the middle group of plateaux (P_5 and P_6) is produced by benzyl cyanide but not by benzonitrile. The work started with these solvents should be extended by using higher members of the same homologous series and related compounds having substituents on the phenyl group.

5.2 Comparison of the gas-chromatographic method of studying ammines with other methods

The tensimetric, indirect and gas-current saturation methods mentioned in 1.3 have been applied by other authors only to the study of complexes formed by gases with solids. In the present work, only a few experiments have been made with solid salts, and their results are insufficient to permit an evaluation of the gas-chromatographic method for studying ammine formation by such salts. It appears from the results obtained with lead bromide and lead chloride that salts should be supported in thin layers, not used in granular form.

For salts in solution that react with ammonia to form a precipitate, the gas-chromatographic method has been more thoroughly tested, and a few exploratory tensimetric experiments have been made. The most striking contrast between the gas-chromatographic and tensimetric techniques lies in their widely differing speeds - it takes about 2 hours to obtain a chromatogram, but several days to obtain a tensimetric curve. The high speed of gas chromatography is a practical advantage, but introduces undesirable rate effects, such as variation of y with sample size and sometimes of plateau height with flow-rate. Tensimetry may yield good equilibrium values on account of the long duration of the experiments, but this feature renders the technique unsuitable for investigating systems that change on ageing. For most salt-solvent systems, gas chromatography has been found to yield reproducible values of dissociation pressures, but less success has been obtained in determining ammine composition. This is largely due to variation of y with sample size and more work is necessary to determine under what conditions y has true stoichiometric significance. However, some of the difficulty in determining ammine composition results from uncertainty about the amount of ammine-forming substance in the column, because there is evidence that the salt in certain packings decomposes or undergoes other changes.

Although the indirect and gas-current saturation methods of investigating ammines have not been tested for salts in solution, they are unpromising for this application. Neither gives any information on ammine composition, which has to be separately determined by analysis. The choice of a liquid for the indirect method is severely limited by the requirements that it should not react with or dissolve either the salt or its solvent; furthermore, the method would probably prove to be as slow as tensimetry. For the gas-current saturation method, a large quantity of ammine would be necessary to ensure saturation, which is a disadvantage if the salt is expensive.

Thus gas chromatography and tensimetry appear to be the most suitable methods for investigating ammine formation by salts in solution; possibly complementary use of both methods will provide most information on such reactions.

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