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Chromatography in a Stream of Water Vapour

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Methods of gas chromatography using water vapour as carrier gas, various ways of generating water vapour and its mixtures with other gases, and also the usefulness of various detecting systems are surveyed. The effect of water vapour on the retention and on the form of the chromatographic zones is analysed in detail. Use of a vapour eluent shows promise in preparative gas chromatography. The bibliography contains 64 references.

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I. INTRODUCTION

One of the principal directions in the development of gas chromatography is the improvement of methods for controlling the sorption properties of columns, by (i) modifying solid supports in order to eliminate the effect of adsorption on the form of the elution zones of (especially strongly polar) sorbates, (ii) modifying adsorbents to change the form (usually to straighten) the sorption isotherms of separable compounds, and also to decrease the sorption coefficients of substances having high boiling points, (iii) increasing the solubility of sorbates in the gas phase, and hence diminishing their partition coefficients between stationary and mobile phases, and (iv) using mixed stationary liquids in order to regulate the degree of separation of components of complicated mixtures.

The use of water vapour as mobile phase is an extremely effective procedure for controlling sorption characteristics in the above ways. In gas–liquid chromatography, water vapour interacts with active centres in the solid support, and may also form binary systems with stationary liquids whose composition is regulated by the use of mixed eluents. In gas-adsorption chromatography the blocking of adsorption centres by water molecules ensures more symmetrical sorbate peaks, together with substantial acceleration of the analysis. Conditions can also be chosen under which an aqueous layer, which acts as sorbent in the chromatographic process, is formed on the adsorbent (or inert support). Finally, the solubility of sorbates in the mobile vapour phase can be increased to a certain extent by raising the pressure in the column.

Use of a vapour eluent also has other advantages—(*a*) the possibility of working both with some detection systems for gas chromatography (catharometer, flame-ionisation detector, etc.) and with systems which detect in the liquid phase, (*b*) cheapness, enabling this eluent to be used in high-output preparative apparatus and works chromatographic equipment, and (*c*) the possibility of complete condensation of the eluate without the use of low temperatures, which almost completely eliminates loss of material in the traps of chromatographic equipment.

The impossibility of analysing readily hydrolysable substances, of course, imposes a significant limitation on the use of water vapour. Furthermore, the danger of condensation imposes a temperature restriction.

The advantages of water vapour as a mobile phase, resulting from the possibility of modifying the solid support, were realised in 1958 by Knight[1], who, on saturating helium as carrier gas with water vapour, observed an increase in symmetry of the chromatographic zones of alcohols, amines, and water. Similarly, in 1964 Kolesnikova et al.[2] worked with moistened helium and obtained symmetrical water peaks. It was noted in particular that moistening the helium changes the sequence of elution of water and butanol. Still earlier, in 1957, Turkel'taub et al.[3] saturated the air carrier gas with water vapour in order to study the effect of the moisture content of silica gel on the chromatographic separation of gases. Water vapour was first used directly as eluent in 1960[4] (this was a continuation of earlier work[5] in which the eluent was alcohol vapour). Photocolorimetric detection was used. At the same time (1960) a Japanese patent was issued[6] on the use of water vapour as mobile phase, and a similar method was described later[7].

In 1964 Davis et al.[8], using a mixture of helium and water vapour as mobile phase, achieved a sensitivity of $2 \times 10^{-6}\%$ of ethanediol with the use of a flame-ionisation detector. Similarly, a mixture of nitrogen and water vapour was used to analyse aqueous solutions of organic acids[9]. Lowering the column temperature with a mixture of water vapour and helium results in a layer of water forming on the solid support; this serves as stationary phase for separating both polar and non-polar substances[10-12]. Beginning in 1967 Nonaka published a series of investigations on chromatography in water vapour using a flame-ionisation detector[13-22]. Mixtures of n-alkanes, aromatic hydrocarbons, alcohols, amines, aldehydes, acids, etc. were analysed, including aqueous emulsions and suspensions of concentration $10^{-2}-10^{-4}\%$. Fig. 1 shows some of the chromatograms obtained in these researches. Similar materials were analysed by Rudenko and his coworkers[23,24].

In a later paper Nonaka [21] added formic acid and hydrazine hydrate to the water vapour in order to block adsorption centres on the solid support more completely when analysing aliphatic acids and alkylamines (by analogy with a principle suggested by Knight [1]). Zhukhovitskii and his coworkers [25-27] have shown the suitability of water vapour for determining impurities in water and in salt solutions. They developed a two-stage method involving the use of a column on which water vapour is sorbed better, and a second column in which it is sorbed worse, than the impurities to be determined. Use of a flame-ionisation detector enables a sensitivity of 5×10^{-7}% to be achieved. The present Reviewers have investigated [28] the chromatographic separation of substances under steam pressures of 1–8 atm in the column. Raising the pressure tended both to shorten the analysis and to give more symmetrical peaks of polar sorbates (Fig. 2).

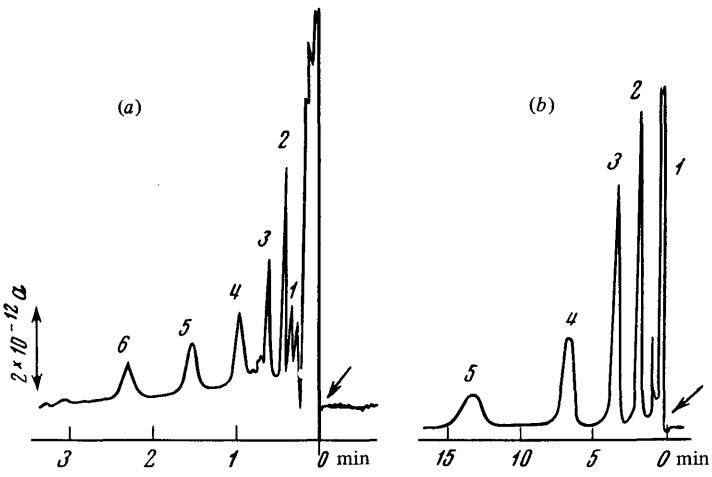


Figure 1. Chromatograms of solutions of polar compounds obtained in a flow of water vapour [20].
(*a*) Glass column of length 2.6 m and internal diameter 2.2 mm filled with firebrick (LBK-28) modified with hydrogen fluoride, with a stream flow of 71 ml min^{-1} at 130°C: 1) methanol; 2) ethanol; 3) propan-1-ol; 4) n-butanol; 5) n-pentanol; 6) hexanol.
(*b*) Glass column of length 2.6 m and internal diameter 1.8 mm filled with Chromosorb PAW with 3% of ortho-phosphoric acid and a steam flow of 42 ml min^{-1} at 170°C: 1) solvent (carbon tetrachloride); 2) lauric acid; 3) myristic acid; 4) palmitic acid; 5) stearic acid.

In 1973 Mar'yakhin and one of the present Reviewers [29], Rudenko et al. [30,31], and also Klesment [32] used water vapour as eluent in preparative gas chromatography.

Conditions for the separation of substances in a stream of water vapour or its mixtures are given in the Table.

II. PREPARATION OF MOBILE PHASE

A mixed eluent can be generated by saturating a gas with water vapour by passing the former either through a moistened granular layer [1] or over the surface of water [9]. A mixed eluent can be obtained also by bubbling through a thermostatted water layer [10]. Helium was passed [1] through a tube 0.6 m in length and 6 mm in diameter immersed in a water bath; the tube was filled with moistened C-22 support, and the relative humidity of the gas at the outlet from the column was ~50% at room temperature. A current of nitrogen entered [10] the lower part of a thermostatted steel vessel, in which it bubbled through a layer of water; the temperature of the vessel was 70 to 95 ± 0.1°C, and that of the tube connecting it with the chromatograph injector was 100°C.

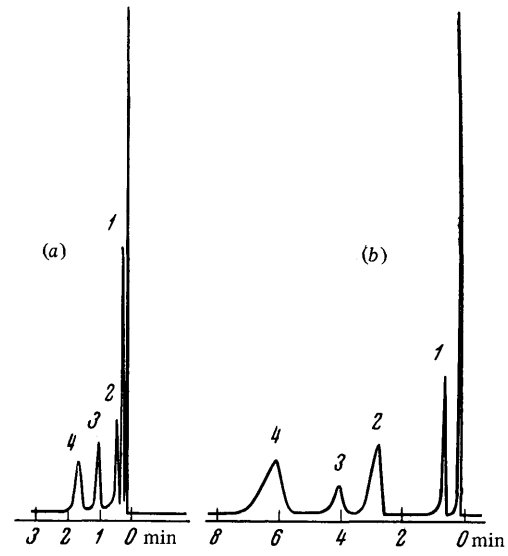


Figure 2. (*a*) Chromatogram of a mixture of normal alcohols and aniline obtained at 125°C on a column of length 0.7 m and internal diameter 2.9 mm filled with high-vacuum silicone grease applied to Chromosorb W: 1) hexanol; 2) aniline; 3) nonanol; 4) decanol.
(*b*) Chromatogram of a mixture of dialkyl phthalates obtained at 170°C on column (*a*): 1) dimethyl; 2) di-isobutyl; 3) dibutyl; 4) di-isopentyl.

Fig. 3*a* represents the system for obtaining a mixed eluent used by Mori and Arimoto [9]. The steam generator was a horizontal thermostatted cylinder half filled with water. Nitrogen passed over the water and entrained the vapour above its surface.

Fig. 3*b* illustrates equipment for generating pure water vapour [4]. Water from the reservoir *1* was transferred at 0.075–0.05 ml min^{-1} by the pump *2* through a microheater *3* comprising a stainless-steel U-tube of length 30 cm and diameter 4 mm placed in a metal cylinder. The column was covered throughout its length with asbestos string, on which was wound nichrome wire. From the microheater the vapour entered a glass chromatographic column, at the outlet from which it condensed and was guided to the detector.

Conditions of separation in a stream of water vapour or its mixtures.

Compounds	Eluent	Sorbent	Column temp., °C	Detectors*	Ref.
Alcohols, water, alkylamines	He sat. with H_2O; He sat. with (H_2O + amine)	di-isodecyl phthalate, tricresyl phosphate, triethylene glycol, $\beta\beta'$-oxydipropionitrile on firebrick; 10% polypropylene glycol on firebrick; 10–40% Silicone DS-550 on firebrick	60	ca	1
Phenol, cresols, 2,4-xylenol, thymol, carvacrol, guiacol, eugenol	steam	glycerol, cholestrol, silicon grease on brick	115, 120, 150	ph	4,33
n-Alcohols(C_{12}, C_{14}, C_{16}); *NN*-dimethylbenzylamine	steam	5% Silicone SE-30 on diatomite	200	–	34
Alcohols (C_1–C_5), water	He sat. with H_2O	30% polyethylene glycol 600 on brick	100	ca	2
Aqueous glycols	He + H_2O	hexaphenyl ether on Teflon	110, 150	fi	8
n-Alcohols (C_1–C_5), glycols, menthol (extracted with alcohol from cigarette smoke)	N_2 + H_2O	H_2O on Gas Chrome CLZ and on silanised Chromosorb W	70–94	fi	10
n-Alkanes, formates, aldehydes, amines, alcohols (study of thermodynamics of dissolution in water)	He sat. with H_2O	H_2O on Chromosorb	20, 30, 40	fi	54
Aqueous (0.01%) alcohols, aldehydes, ketones, esters	steam	HF-modified firebrick; Isolite (50% SiO_2)	110–210	fi	13
Polyalcohols, organic acids, phenols, amines	steam	KF- or H_3PO_4-modified brick; Chromosorb P with 3% H_3PO_4; MgO	100–270	fi	14
Aliphatic acids (C_2–C_{18}); dil. aq. benzoic, salicylic, lactic acids	steam	Chromosorb P with 3% H_3PO_4	135–230	fi	15
Phenol, cresols, 2,4-dimethylphenol, *p*-ethylphenol, *p*-t-butylphenol (dil. aq. solns.)	steam	Chromosorb PAW with 3% H_3PO_4	135–205	fi	16,20
Pentane solns. of C_{10}–C_{14} n-alkanes	He sat. with H_2O at 20°C	46% H_2O on Chromosorb P	20	fi	11
n-Alkanes (C_{10}–C_{18}, C_{24}), octane isomers	He sat. with H_2O at column temp.	4–46% H_2O on Chromosorb P; 10% H_2O on Porasil C treated with HNO_3 + H_2SO_4 and washed to neutrality	20–85	fi	12
n-Alkanes (C_1–C_6), benzene, toluene ($\geqslant 5 \times 10^{-7}$% in H_2O and salt solns.)	steam	hydrophobic silica gel; activated carbon BAU; Apiezon L on Celite 545	110–180 (programmed)	fi	25,26, 27
Aqueous (0.5–0.02%) acids—aliphatic C_6–C_{18} and dicarboxylic, iso- and tere-phthalic, citric	N_2 + H_2O	diatomitic solid support (Shimalite AW) treated with 1.5% H_3PO_4	230–290	fi	9
n-Alkanes (C_5–C_9), benzene, toluene, isomeric xylenes, ligroin (as 0.1–10^{-4}% aq. emulsion)	steam	alumina	110–260	fi	17,19, 20
Naphthalene, 1- and 2-methylnaphthalenes, anthracene, chrysene, terphenyl, triphenylene, biphenyl, quaterphenyl (as 0.01–10^{-4}% aq. emulsion or suspension)	steam	Chromosorb PAW	130–260	fi	18,20
N-Alcohols (C_1–C_6), aldehydes, ketones, ethers, alkylamines, pyridine, aniline, toluidine, glycols, C_2–C_{18} aliphatic acids and esters, dicarboxylic acids	steam	diatomitic brick modified with HF, KF, or KHF_2; diatomitic brick ignited after addition of H_3PO_4; ignited MgO	110–260	fi	20
Aliphatic acids (C_2–C_{18}), alkylamines (C_3–C_{18}), ethylenediamine, aminoethanol	steam + 10% formic acid; steam + 20% hydrazine hydrate	Corning GLC-100 porous glass beads, Chromosorb GAW	125–200	fi	21
n-Alcohols (C_6–C_{10}), di-isoalkylamines, aniline, benzylamine, dimethylaniline, ethylaniline, diethylaniline, aliphatic acids (C_2–C_6) (including 0.05% aq. solns.)	steam	10% polyethylene glycol 4000 on Chromaton; 10% polydimethylsiloxane SKTV-1 on Chromaton	150	fi	24
n-Alkanes (C_{10}–C_{15}), di-isoalkylamines, benzylamine, mono- and di-methyl- and -ethyl-benzylamines (preparative isolation)	steam	SKTV-1 polydimethylsiloxane on Chromaton; polyethylene glycol adipate on Chromosorb A	130–210	fi	30,31
Alkanes, alkylbenzenes (preparative isolation)	steam; N_2 + H_2O	25% polyethylene glycol adipate on Spherochrome-1	120–140	fi	29
Coal tars (preparative separation)	steam	21% Apiezon L on Rysorb C (flow from fractionating column)	programmed at 20–55 deg h^{-1}		32

*Detectors: ca = catharometer; ph = photocolorimeter; fi = flame-ionisation detector.

In the apparatus used by Nonaka [13–21] (Fig. 3*c*) one stage in the preparation of the eluent was purification of the stream over copper oxide at 500–600°C.

The Reviewers used the arrangement in Fig. 3*d* to examine the chromatographic behaviour of substances under high pressures of water vapour. Nitrogen from a cylinder entered the upper part of a vessel half filled with distilled water. From here the nitrogen pressure transferred water to a tube located in the thermostat and filled with metal turnings to increase the evaporating surface. The resulting water vapour passed through a buffer vessel to diminish fluctuations in the flow rate, and entered the chromatographic column, in which the required pressure was established by means of a capillary at the outlet. Most of the water vapour then escaped into the atmosphere, and only a small quantity entered the flame-ionisation detector. The flow of water vapour through the column could be regulated by varying the pressure of the nitrogen entering the vessel *7*.

In 1962 standard equipment was advertised for generating steam for use in gas chromatography [34]. The device comprised a steel boiler containing an electric heater and fitted with a safety valve. Steam production reached 1 litre min^{-1} at pressures up to 3 kg cm^{-2}. Mixtures of water vapour with nitrogen of controllable composition could also be obtained.

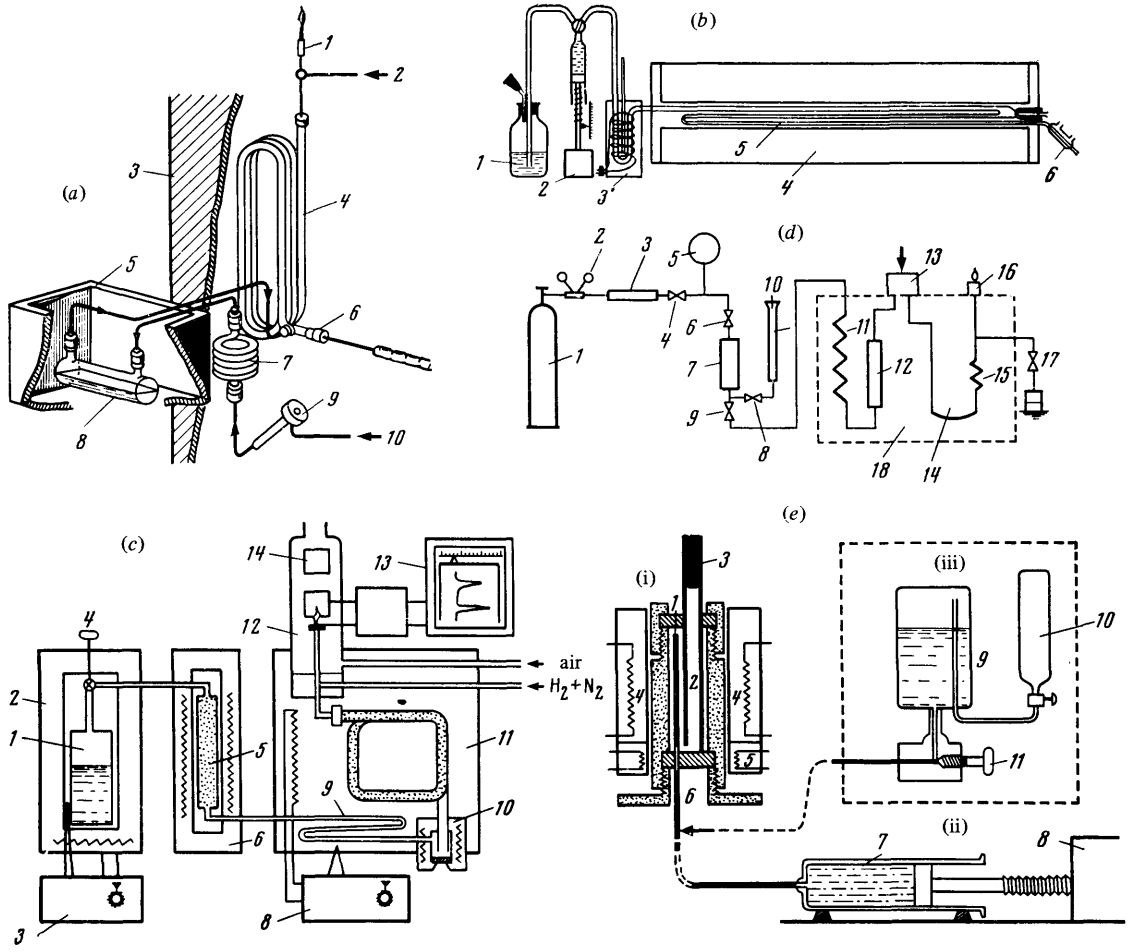


Figure 3. Diagrams of types of chromatographic apparatus. (*a*) Apparatus for operations with mixed eluent [9]: 1) flame-ionisation detector; 2) hydrogen; 3) thermostat for columns; 4) glass column; 5) thermostat for steam generator; 6) sample introduction; 7) helical tube; 8) steam generator; 9) unit for admission of carrier gas; 10) carrier gas. (*b*) Apparatus for chromatography in a flow of water vapour [4]; 1) water reservoir; 2) pump; 3) steam microgenerator; 4) thermostat; 5) glass column; 6) condenser. (*c*) [Alternative] apparatus for chromatography in flow of water vapour [13-20]: 1) steam generator; 2) electrical heater for generator; 3) thermoregulator for generator; 4) needle valve; 5) column containing CuO; 6) CuO column heater; 7) air thermostat; 8) thermostat controller; 9) buffer for water vapour; 10) introduction of sample; 11) analytical column; 12) flame-ionisation detector; 13) recording system; 14) hygrometer. (*d*) Apparatus used by Reviewers: 1) nitrogen cylinder; 2) high-pressure regulator; 3, 4, 6, 8, 9, 17) needle valves; 5) standard manometer; 7) vessel containing distilled water; 10) funnel for filling (7); 11) preliminary column filled with metal turnings; 12) buffer vessel; 13) introduction of sample; 14) chromatographic column; 15) capillary; 16) flame-ionisation detector; 18) thermostat. (*e*) Apparatus for generating mixtures of water vapour with formic acid and with hydrazine hydrate [21]: i) evaporator; ii) liquid pump; iii) alternative solution feed system; 1) eluent evaporator; 2) point of introduction of sample; 3) analytical column; 4) electrical heaters; 5) electrical heater for membrane; 6) capillary for feeding eluent; 7) glass syringe; 8) driving mechanism; 9) vessel containing water or solution; 10) gas cylinder; 11) needle valve.

Nonaka [21] used a modified chromatograph evaporator (Fig. 3*e*) to evaporate mixtures of water with formic acid and hydrazine hydrate. The Reviewers varied the pH of water vapour by placing aqueous formic acid and ammonia of various concentrations in vessel 7 in Fig. 3*d*.

The flow of the vapour eluent in the column was not measured directly in several investigations, owing to the difficulties encountered. Nonaka [20] used a specially designed hygrometer to determine the flow of water vapour. The weight of water G (in g min^{-1}) condensed at the outlet from the column has been measured [29], and hence the flow of vapour calculated by means of the equation

$$V_a = \frac{G \cdot P \cdot v}{P_0} \qquad (1)$$

where v is the specific volume of the vapour at pressure P in the column and the temperature of the column, and P_0 is the atmospheric pressure.

The Reviewers made preliminary use of an ordinary carrier gas to measure

$$C = \frac{V_\alpha j t_{0i}}{g} \quad (2)$$

where V_α is the speed of the gas leaving the column at the temperature of the latter, t_{0i} the retention time of the unsorbed substance, g (g) the weight of the stationary liquid or the adsorbent, and j the pressure gradient factor. The specific retention volume with the vapour eluent was then calculated by means of the formula

$$V_g^T = \left(\frac{t_R}{t_0} - 1\right) \cdot C \quad (3)$$

where the retention times of sorbate and unsorbed substance t_R and t_0 were measured in a stream of water vapour. In both cases methane was used as unsorbed substance.

III. DETECTION

Several of the usual chromatographic detectors are entirely suitable for working with water vapour. Knight [1] used a catharometer to detect substances in a flow of helium saturated with water. Comparison of the thermal conductivity of water vapour with those of other substances indicates that a catharometer can be used with chromatography in water vapour provided that the flow is sufficiently accurately stabilised to avoid fluctuations. Apparently a density balance can also be used in work with water vapour. The temperature of the detectors should, of course, be such as to exclude the possibility of condensation of the vapour.

An argon detector is obviously unsuitable for work with water vapour [35,36]. It was shown [37] that a tenfold increase in the concentration of water in argon (from 10^{-5} to 10^{-4} vol.%) diminishes the sensitivity of the detector by 75%. The permissible concentration of moisture in the gas for a helium detector is 10^{-4}%. [38] The range of linearity of the detector readings becomes shorter with increase in the concentration of water.

A flame-ionisation detector is most suitable with chromatography in water vapour, since it is only slightly sensitive to water. This detector has almost invariably been used with this eluent. Although the signal of a flame-ionisation detector for water is very small, it is considered to exist [39]. Water present in a sample influences the sensitivity of a flame-ionisation detector to substances eluted with it [40]. However, Amirov et al. have found [41] that the sensitivity of such a detector to water is 0.01–0.001% of its sensitivity to benzene, a conclusion confirmed by another worker [42]. The background current of a flame-ionisation detector doubles with increase in the concentration of water in argon from 10^{-4} to 1%. [43] Nevertheless, increasing the concentration of water in argon by a factor of 10^4 (from 10^{-6} to 10^{-2} vol.%) diminishes the sensitivity of the detector to ether by only 29%. When the oxygen supplied to the detector burner was saturated with water at various temperatures [44], saturation up to 12.2 mole % lowered the sensitivity of the detector by 18.7%. Water can be determined by using carbon monoxide instead of hydrogen in the flame-ionisation detector, whose sensitivity is improved by adding small quantities of water or hydrogen to the carbon monoxide. Thus the above results justify the use of a flame-ionisation detector in chromatography using water vapour as eluent. The decrease in sensitivity in the presence of water vapour is so small that very dilute ($5-10 \times 10^{-7}$%) solutions of organic substances can be analysed [20,26]. Nonaka [20] used additional preheating of the detector to avoid condensation of water vapour in the burner. A flame-ionisation detector made of glass [46] has been used [24]. Furthermore, detectors based on automatic titration of the eluate may be suitable for work with a vapour eluent [47].

IV. EFFECT OF WATER VAPOUR ON THE RETENTION AND ON THE ZONE PROFILES OF THE CHROMATOGRAPHED COMPOUNDS

No exhaustive theory has been published to describe the effect of water vapour on the retention and the spreading of chromatographic zones. However, existing results show that water vapour can successfully be used as mobile phase both in gas-adsorption and in gas–liquid chromatography. In the former the water blocks certain active centres of the adsorbent, tending to straighten the sorption isotherms of the test substances. If the stationary liquid in gas–liquid chromatography does not dissolve water, the effect of water vapour is to modify the solid support. In these cases competitive adsorption occurs between water vapour and the test sorbates, the former usually being the more strongly adsorbed, so that elution is accompanied by a displacement effect. Fig. 4 shows as example chromatograms obtained [34] for a mixture of alcohols, with water vapour and nitrogen as eluent. This phenomenon is not observed, of course, if the support or the adsorbent is hydrophobic. The dissolution of water in the stationary liquid produces a binary stationary phase, whose ability to sorb the test substances can be controlled by varying the water content (by varying the temperature, the water vapour content of the mixed eluent, or the pressure).

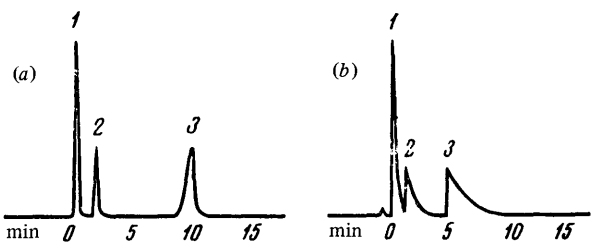


Figure 4. Chromatograms obtained [34] on column containing 5% Silicone SE-30 on diatomite at 200°C with different carrier gases (pressure at inlet 1.4 kg cm^{-2}): *a*) stream; *b*) nitrogen for n-alcohols: 1) dodecyl; 2) tetradecyl; 3) hexadecyl.

Measurements have been made in the Reviewers' laboratory [29] of the linear retention index of aromatic hydrocarbons on a column containing 25% of polyethylene glycol adipate on Spherochrome-1 with nitrogen and steam eluents at various temperatures. The change to water vapour produced a significant increase in the retention indices, especially at lower temperatures: at 130°C the indices of the aromatic hydrocarbons in water vapour exceed those in nitrogen by 1–1.5, which corresponds to 100–150 on Kováts logarithmic scale. This increase is due to the shortened retention times of the n-alkanes used as standards. A similar increase

in the logarithmic retention indices of polar compounds has been observed[24] in water vapour at 150°C, the shift amounting to 50–80 for organic acids. The composition dependence of linear retention indices for a mixed eluent (nitrogen plus water vapour) was almost linear[29].

The replacement of nitrogen by water vapour and dissolution of the latter in the stationary phase leads to a change in form of the sorption isotherms[29]. Whereas with nitrogen the peaks for aromatic hydrocarbons were usually blurred mainly at the tail (provided that samples were sufficiently large), predominant spreading of the front was observed in water vapour. The peaks of n-alkanes, characterised by spreading of the front, became still more unsymmetrical on passing to water vapour. Thus the form of the chromatographic peaks can be controlled by varying the composition of the eluent. With small samples the efficiency of a column operating with steam is quite high. According to Nonaka[20] the height equivalent to a theoretical plate may be 1–2 mm, the optimum speeds of the mobile phase being almost the same as with the usual eluents.

When the column is filled with a solid support at a temperature below the dew-point, a layer of water is formed on the support, and serves as mobile "stationary" phase for separating mixtures. Volatile solvents were first used as "stationary" phases in 1958.[48] Porter and Johnson[49] studied the behaviour of volatile solvents as mobile and liquid phases under conditions of circulatory chromatography. In a detailed study of the behaviour of mobile organic liquid phases in gas chromatography[50,51] heptane, benzene, ethanol, and other compounds served as both gas and liquid phases. These compounds have recently been used as mobile phases[52,53]. Water has served simultaneously as vapour and liquid phases[10-12,54]. Phifer and Plummer[10] analysed polar compounds with good solubility in water, which ensured considerable retention of them in the column.

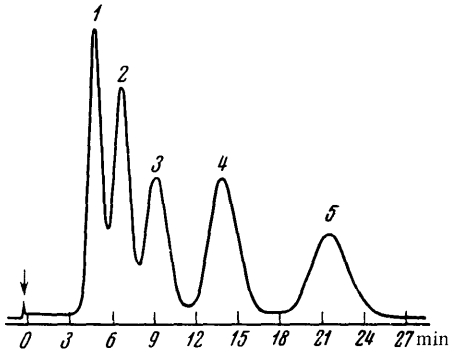


Figure 5. Separation of C_1–C_5 n-alcohols in a flow of a mixture of nitrogen and water vapour[10] at 70°C: 1) pentanol; 2) butanol; 3) propanol; 4) ethanol; 5) methanol:

It is interesting that, since water interacts by means of hydrogen bonds with alcohols undergoing analysis, the elution sequence observed is opposite to the usual order (Fig. 5). Karger et al.[11,12] investigated the behaviour of non-polar sorbates, which, being almost insoluble in water, were eluted very rapidly from the column. The relative rate of elution of alkanes on a column with water exceeded those on columns with Apiezon and with polyethylene glycol by factors of 30 000 and 67 respectively. On a column with water n-tetracosane is eluted even at 85°C, which is 306 deg below its boiling point (the vapour pressure of n-tetracosane at 85°C is 2×10^{-4} mmHg). In the separation of n-alkanes the ratio of the degree of separation to the duration of analysis on a column with water at 20°C exceeded that on a column with squalane by a factor of 12. This confirms the conclusion[55,56] that the rapidity of analysis of non-polar compounds is increased on passing to polar stationary phases. Karger et al. showed that the activity coefficients of n-alkanes in water are of the order of 10^6. According to Pecsap and Martin[54] these quantities for C_5–C_7 n-alkanes are $(1-8) \times 10^3$ at 20°C. These workers studied also the thermodynamics of the dissolution in water of various other organic compounds, including alcohols, aldehydes, and chlorinated methanes.

Water was used as stationary liquid in earlier work[57,58] to separate chlorinated methanes at 20°C. Here, however, a dry carrier gas was used initially. Varying the percentage impregnation of kieselguhr with water led to a change in the elution sequence of the sorbates.

Giddings et al.[59,60] studied the effect of surface-active additives on the efficiency of a column with water deposited on glass beads. The carrier gas was moistened helium. Experiments at 2°C showed that a small addition to water of a surface-active agent, in particular hexadecanol, led to marked broadening of the sorbate peak owing to the additional resistance to mass transfer at the surface.

V. PREPARATIVE GAS CHROMATOGRAPHY

The use of water vapour and its mixtures in preparative gas chromatography is extremely promising, since it will lower the economic cost, enable the selectivity of the column to be controlled, and also ensure complete recovery of the separated substances. In particular, water vapour and its mixtures with organic vapours will ensure complete condensation of the eluate after passing through the column even at ordinary temperatures by the use of running water as coolant[29]. Such a procedure enables losses of separable substances to be almost eliminated, and of course is preferable to published methods[61-63] of the low-temperature condensation of argon and carbon dioxide emerging from the column.

It is interesting that, if the eluent is a mixture of water vapour and the vapour of a water-insoluble organic compound, condensation of the eluent in the trap is followed by extraction of the separable substance, which condenses in one of the phases (aqueous or organic). Thus the proportions of the components of the mobile phase (water vapour and organic eluent) should be chosen, depending on the nature of the separable substances, to ensure that the latter is concentrated sufficiently.

Preparative isolation of individual aromatic hydrocarbons has been accomplished[29] on a column of internal diameter 20 mm and length 3.2 m containing 25% of polyethylene glycol adipate on Spherochrome with water vapour and its mixtures as carrier gas. Hydrocarbons and polar compounds have been isolated[30,31] in a flow of water vapour on columns of a silicone and of polyethylene glycol acetate. It has also been reported that water vapour may be used in projected industrial chromatographic equipment, which would eliminate the eluent recirculation and fine purification system[64].

An original method for the preparative separation of complicated mixtures by combining fractional distillation with chromatography in a stream of water vapour has been suggested by Klesment [32]. The separable mixture (coal or shale tar) was run into the still of a fractionating column and steam-distilled, with the flow from the upper part of the column (of height 40 cm and efficiency 7–10 theoretical plates) continuously entering a chromatographic column of length 2.8 m and internal diameter 12 mm containing 21% of Apiezon L on Rysorb C operating with temperature programming. Narrow fractions (0.2–1 ml) were collected in vacuum receivers (residual pressure 50 mmHg) at equal time intervals. Fractions boiling up to 400°C were isolated by the above method.

Thus the use of water vapour as mobile phase represents a definite stage in the development of gas chromatography.

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