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Institute of Organic Chemistry,
Academy of Sciences of the
Ukrainian SSR.

ANALYSIS AND SEPARATION OF AROMATIC HYDROCARBONS BY GAS–LIQUID CHROMATOGRAPHY

V. I. Dal' and V. M. Nabivach

The rapid development of gas–liquid chromatography since 1952, when it was introduced by James and Martin, is undoubtedly due to its high analytical precision, to its speedy and reliable separations, and to the ease with which it can be applied to the automatic control of industrial processes.

The separation of a mixture in gas–liquid chromatography arises from the different rates of motion of the components along the layer of stationary phase, resulting in the formation of separate zones or bands. Thus the rate of movement of the bands and the dependence of band width on various experimental parameters form the main subject of the theory of gas chromatography[1-22]. The theories which have been put forward to explain the motion and the spreading of bands fall into three distinct groups. The first group includes the theory of theoretical plates[23-33], which discusses the chromatographic column as a plurality of elementary sections (theoretical plates), in each of which an equilibrium between the liquid and the gas is set up. No such equilibrium can exist in practice, whatever the length of column considered. The second group includes the various kinetic approaches[34-39] to the chromatographic process, based on considerations of molecular motions. These leave out of the picture all macroscopic characteristics. The third group is called the "theory of rates" or "theory of macroscopic constants"[40-46] and appears to be the most rational of the three. It describes the spreading of bands in terms of macroscopic parameters, such as diffusion coefficients, mass-transfer coefficients, etc.

Many articles and monographs have been devoted to the effects of particular factors on the efficiency of separation[47-72,235], and much attention has been given to the use of gas chromatography in the separation and analysis of various classes of organic compounds: saturated and unsaturated hydrocarbons[73-84], halogenated compounds[85-88], phenols[89-92], sulphur compounds[93-95], fatty acids and esters[96-99], amino and nitro compounds[100-105], lubricating oils[106-107], pyridine bases[108-109], products from oil refin-

ing[110-113], low-boiling gases[114-116], and others[117-121].

The most complex mixtures, and the most difficult to separate, are encountered in the petroleum and petro-chemicals industries. Among these must be included mixtures of aromatic hydrocarbons, and many publications have been devoted to the analysis and separation of such mixtures[122-146].

The growing volume of production of synthetic materials demands continuous improvements in the efficiency of the methods for producing raw materials, such as *p*-xylene. In this connection the gas–chromatographic separation and analysis of the xylene isomers offers an accurate and progressive method, which enables substances boiling within 0.1° of each other to be separated.

A detailed discussion of recent publications on the separation of the isomers of xylene will be given below.

Keulemans, Kwantes, and Zaal, in their study[147] of the influence of the stationary phase on the selectivity with which various hydrocarbons, including aromatics, were separated, found that fluorene picrate was highly selective towards aromatic compounds. This may be due to the formation of a molecular complex or of a primary addition product between solvent and solute in a picric acid–fluorene solution. The effect of temperature on the separation of *m*- and *p*-xylene was investigated by Vaughan[148], who showed that the separation was improved by lowering the temperature from 140° to 60°. Jentzsch and Bergmann[149] studied the relation between relative retention times and relative vapour pressures for a mixture of aromatic hydrocarbons containing xylene isomers. Whitham[150] analysed industrial xylene in a column packed with a stationary phase of fluorene picrate. Zlatkis, O'Brien, and Scholly[151] used a stationary phase of benzyldiphenyl in their analysis of aromatic hydrocarbons. Langer, Zahn, and Pantazoplos[152], who also separated the isomers of xylene, took advantage of the difference in their coordination electron-transfer behaviour, which involves "charge transfer" forces[153]. To this end, they used tetrahalogenophthalates, containing many electronegative substituents in the aromatic nucleus. As a result of the formation of complexes between the aromatic compounds and the substituted tetrahalogenophthalates[154,155], they succeeded in inverting the usual elution sequence, and detected *m*-xylene before the *p*-isomer. Zlatkis, Ling, and Kaufman[156] introduced many new polar compounds, such as 1-halogenonaphthalenes,

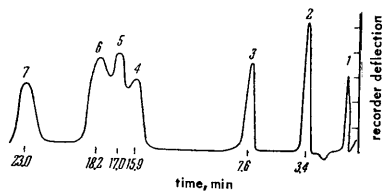


Fig. 1. Separation of aromatic hydrocarbons on a packed column[161]: 1) air; 2) benzene; 3) toluene; 4) ethylbenzene; 5) *p*-xylene; 6) *m*-xylene; 7) *o*-xylene.



Fig. 2. Separation of aromatic hydrocarbons on a capillary column[161]: 1) benzene; 2) toluene; 3) ethylbenzene; 4) *p*-xylene; 5) *m*-xylene; 6) *o*-xylene.

Separation of aromatic hydrocarbons by gas-liquid chromatography.

Composition of mixture to be Separated	Column dimensions (cm) and experimental temperature (°C)	Stationary phase	Flow rate of carrier gas	Sample size	Column efficiency in theoretical plates	Separation coefficient* for *m*- and *p*-xylene	References
Benzene, toluene, ethylbenzene, *o*-, *m*-, and *p*-xylene	183×0.4 80°	dinonyl phthalate, 31%	N_2, 20 ml min^{-1}	10 μl			122
Acetone, n-octane, 2-methyloctane (isononane), benzene, ethylbenzene, toluene, *o*-, *m*-, *p*-xylene	180×0.6 120°	fluorene picrate, 28%	N_2, 33 ml min^{-1}				147
Benzene, cyclohexane, ethylbenzene, toluene, *o*-, *m*-, and *p*-xylene	330×0.4 78.6°	paraffin wax, 28%	N_2, 42 ml min^{-1}	0.5 mg	2000	1.008	126
Paraffins, ethylbenzene, *o*-, *m*-, and *p*-xylene	830×1.27 110°	fluorene picrate	N_2, 13.3 ml min^{-1}	0.5 ml	2000		150
Benzene, toluene, ethylbenzene, *o*-, *m*-, and *p*-xylene	244×0.6 50°	1-chloronaphthalene, 15%	H_2, 220 ml min^{-1}		2500	1.060	156
Toluene, ethylbenzene, decane, *o*-, *m*-, and *p*-xylene	889×0.5 95°	di-n-propyl tetrachlorophthalate, 7%	He 84.8 ml min^{-1}	0.7 μl	7500	0.962	152
Benzene, toluene, ethylbenzene, *o*-, *m*-, and *p*-xylene	500×0.5 100°	benzyldiphenyl, 15%	He 100 ml min^{-1}	0.005 ml	9500	1.032	151
Benzene, toluene, ethylbenzene, *o*-, *m*-, and *p*-xylene	1200×0.025 78.5°	7,8-benzoquinoline	N_2 0.7 ml min^{-1}	1 μg	14600	1.030	161
Benzene, toluene, ethylbenzene, *o*-, *m*-, and *p*-xylene	1524×0.22	poly(ethyl glycol dibenzoate), 5%	A	75 μg	30000		157
Ethylbenzene, *o*-, *m*-, and *p*-xylene	4572×0.025 70°	didecyl phthalate, 0.4%	0.43 ml min^{-1}		50000	1.021	159
Cyclopentane, methylcyclopentane, cyclohexane, methylcyclohexane, benzene, toluene, ethylbenzene, *o*-, *m*-, and *p*-xylene	5234×0.025 90°	poly(propylene glycol)	A, 0.5 ml min^{-1}	100 μμl	100000	1.035	160

* The separation coefficient is defined as the ratio of the gas-retention volumes of the two components at the temperature of the experiment, and characterises the ease with which the components can be separated.

which afford a separation of *m*- and *p*-xylene when used as stationary phases. Scott[157] effected the complete separation of xylene isomers on a column of about 30 000 theoretical plates and over 15 m long. Franc and Jokl[158] carried out an analysis of xylenes in a mixture of aromatic hydrocarbons on an apparatus, called by them a spectrochromatograph, in which a gas–liquid chromatographic assembly was combined with a u.v. spectrophotometer. Golay[159] achieved a separation of *m*- and *p*-xylenes using a 45 m long capillary column, treated with didecyl phthalate. A 52 m capillary column, equivalent to 100 000 theoretical plates, was applied by Condon[160] to the same separation. Desty, Goldup, and Swanton[161] showed that 7,8-benzoquinoline offers better separation of the xylenes than the previously recommended stationary phases, such as squalane, tritolyl phosphate, and benzyldiphenyl. They carried out parallel separations of benzene, toluene, ethylbenzene, and the xylenes, on a column packed with 20% 7,8-benzoquinoline on kieselguhr, and on a 12 m capillary column, the walls of which were also lined with 7,8-benzoquinoline. Their results are shown in Figs.1 and 2. The choice of stationary phase for separating the isomers of xylene is also discussed elsewhere[162-164].

The conditions and experimental parameters for the analysis and separation of aromatic hydrocarbons are set out in the Table.

Mention should also be made of some interesting analyses and separations carried out on high-efficiency capillary columns[165-171]. Zlatkis and Haufman[172] have described a nylon capillary column, 1.6 km long and of ~ 0.2 cm internal diameter, whose efficiency exceeded 1 000 000 theoretical plates.

Various types of detector have been used for the quantitative and qualitative analysis of aromatic hydrocarbons[173]. In addition to the widely used thermal conductivity cell[150,151,174-176], the micro-flame detector[171-186] and its various modifications[187-189] receive frequent mention, as well as the ionisation detector, which measures the ionisation produced by β-radiation[190], the gas-density balance[191], the ordinary [argon (Ed. of Translation)] ionisation detector[192-196], a detector based on the absorption of u.v. light by the substance flowing through a spectrophotometer cell[197], the flame-ionisation detector[198], the vapour-phase i.r. spectroscopic method[199-201], and others[202-204].

Various foreign firms have produced chromatographic assemblies for the analysis of aromatic hydrocarbons, differing mainly in the type of detector used, the method of gas injection, the control of gas flow, and other details[205-214]. The British firm Shandon[215,216] market a chromatograph which incorporates a detector, designed by Scott[177], with a sensitivity (10^{-3}%) unaffected by the temperature of the experiment up to 375°. W.G. Pye and Co. (Cambridge, England) advertise an argon chromatograph based on Lovelock's ionisation detector[192]. The limit of detection of this instrument is as low as 10^{-11} mole, making its sensitivity tens of thousands of times higher than that of the thermal-conductivity cell. Separations of mixtures of benzene, toluene, ethylbenzene, and xylenes can be accomplished in 15 min on the apparatus marketed by the American firm Barber-Coleman Co.[218], whose ionisation detector relies on tritium as the source of ionisation.

The current trend towards extending gas–liquid chromatography to higher and higher temperatures[219-225] (300°, and even 500°) should enable close-boiling fractions to be separated for subsequent analysis by other methods[226,227].

Large-diameter columns have been built for the separation of moderately large quantities of mixtures of aromatic hydrocarbons on a preparative scale[129,228]. Atkinson and Tuey[229] used a 3 m column of 3 cm internal diameter to separate the constituents of a 30 g sample of purity better than 99.8 wt.%. Automatic methods of sample injection[230,231] and synchronised collection of the wanted fractions[232-234] will lead to practical processes for the gas–liquid chromatographic isolation of difficultly separable components of a mixture.

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F. Dzerzhinskii Institute of
Chemical Technology,
Dnepropetrovsh.

STATISTICAL METHODS OF FINDING OPTIMUM CONDITIONS FOR A CHEMICAL PROCESS

V. V. Nalimov

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I. INTRODUCTION

Problems involving the determination of optimum conditions are frequently encountered in laboratory, pilot-plant, and full-scale studies. Many variables have to be tested in order to find the conditions giving the greatest yield, least cost, highest purity, etc. There is no point in setting out to test all possible combinations of the various factors in such a case, because the number of experiments required would be vast; even if that number were performed, the results from the first ones would not be comparable with those from the last on account of uncontrollable changes in the apparatus and in the reactants. Moreover, the results would be of little practical value, because we do not need to know the effects of the various factors in the yield for conditions far from the best.

In 1951 Box and Wilson [1] proposed a method of finding the best conditions by an application of mathematical statistics to the design of experiments and to the analysis of results. A few tests are made; the shortest route to the optimum region is deduced after each series even though the relation of the yield to the adjustable factors is not known in functional form. As the optimum region is approached, a larger series of tests is planned, and more elaborate methods of analysis are applied in order to deduce the best conditions. The conditions are interpreted by means of models in many-dimensional "factor" space. This method differs from ordinary ones in that the experiments are designed; the number of tests, and the places corresponding to those tests in factor space, are determined from certain mathematical rules. All factors are varied together; the approach is thus different from classical methods, in which only one factor is changed in each test. The differential