GAS CHROMATOGRAPHY

THE third international symposium on "Gas Chromatography" to be organized by the Gas Chromatography Discussion Group, this time in conjunction with the Society for Analytical Chemistry, was held at Edinburgh during June 8-10. More than 560 delegates attended the meeting, of whom more than 160 were from overseas. Three excellent receptions provided by the Organizing Committee, the Lord Provost of Edinburgh and the British Petroleum Co. were held in the evenings. Other items that added interest to the meeting were an instrument exhibition showing recent developments in commercial gas-chromatographic equipment, and visits to local industries arranged for the Saturday following the symposium.

The symposium was divided into three sections, Apparatus and Technique, Theory and Application, and General Applications, each being introduced by a well-known authority in the field. Preprints of the twenty-nine papers read were issued to delegates before the meeting, so authors had to point out only the highlights in their papers, thus giving more time for discussion. The full proceedings, edited by R. P. W. Scott, will be published by Butterworths Scientific Publications later.

The symposium began with a welcoming address by Prof. E. L. Hirst, of the University of Edinburgh, who described the impact chromatography had made on research in recent years. Dr. A. T. James, chairman of the Gas Chromatography Discussion Group, gave the opening address, outlining some of the more significant lines of research being currently followed. A report on the recent activities of the East German Working Group was read by Mr. H. P. Angele.

In the introductory lecture to the first session, "Applications and Technique", R. P. W. Scott pointed out areas where there was still much controversy among gas chromatographers. He emphasized the need for further work on column design, detectors and recording methods to improve both the speed and accuracy of quantitative analysis.

The recent very sensitive hydrogen flame and argon ionization detectors were the subject of the first session. L. Onkiahong and D. H. Desty reported investigations carried out on the flame ionization detector to determine the optimum design and operating conditions. Both concluded that the construction of the detector was not too critical except where the highest sensitivity is required. Similar results were found by R. C. Condon, who in addition compared the two ionization detectors. J. E. Lovelock investigated the design and operating parameters of the family of argon detectors. The triode detector, the most recently introduced, has a sensitivity of 10^{-14} gm./sec., about a hundred times better than that reported for the flame ionization detector. The sensitivity of all the argon detectors was found to be considerably reduced by the presence of trace amounts of hydrogen, nitrogen, oxygen, carbon dioxide and water in the argon. A comparison of integral and differential ionization detectors was made by S. Matousek.

Most of the discussion following the papers centred around the flame ionization detector. Many workers

gave details of their own particular design, and it appeared that thick-walled jets which remained cool were preferable to those that glowed at red heat. F. van der Craats described how the linearity of the detector could be improved by using a cage rather than a disk as the upper electrode, and D. H. Desty stated that a small increase in sensitivity could be obtained by the addition of argon, nitrogen or oxygen to the hydrogen supply.

A disadvantage of the hydrogen flame-ionization over the argon detector is that an expensive impedance converter must be used to measure the low ionization currents produced. L. Onkiahong suggested that it may be possible to overcome this by the use of an a.c. polarizing potential (~ 100 c.p.s.) applied between the jet and a third electrode situated between the jet and collector. By this means a pulsed d.c. signal would be obtained at the collector which could be amplified by conventional methods. J. F. Smith gave details of an inexpensive amplifier using a cathode follower that was adequate where the highest sensitivity was not required.

An important feature not given sufficient attention by the majority of workers investigating detector performance was the determination of response factors for compounds of different type, to see whether any correlation exists between response and molecular structure. Difficulties in obtaining low known concentrations of vapours may be partly responsible for this, and the method for obtaining accurate concentrations down to 10^{-8} molar described by D. H. Desty should enable fuller work to be carried out in the future. Although no simple correlations were found in the papers read, in the discussion R. C. Condon pointed out that for the series of halogen compounds mono-, di- and tri-chloromethane the response of the flame ionization detector was proportional to the amount of hydrogen in the molecule, and F. Schild had found that the weight response for a number of oxygenated compounds was proportional to the product of the peak area and molecular weight. Both H. M. McNair and F. van der Craats compared the response factors that they had determined for hydrocarbons with those obtained by D. H. Desty and L. Onkiahong. A wide variation in relative response factors was apparent, and it may well be that these factors depend very much on the design and conditions under which the detector is operated.

The question of detectors of low concentrations of permanent gases arose, and T. B. Kent described how by using argon containing a few p.p.m. of acetylene as carrier gas concentrations of permanent gases in the p.p.m. region could be detected by the decrease in background signal produced. The use of the gas-discharge tube for the determination of small concentrations of impurity gases in argon was the subject of a paper read by B. Riley, and several industrial applications for an instrument of this type were outlined.

Following the discussion on detectors, attention turned to other developments in apparatus and technique. J. Boeke described the use of a modified form of frontal analysis in which the sample is continuously

introduced into the column considerably diluted in an inert carrier gas, and gave details of a detector arrangement that enabled curves approaching differential rather than the usual integral records to be obtained. I. Halasz described an integrator based on a new principle having a count-rate of 1.8 million pulses per minute for a full-scale recorder deflexion and which may be adjusted to correct automatically for the calibration factor of the substance detected. A comparatively inexpensive high-speed recording system, using a long-persistence cathode-ray oscilloscope, was described by R. P. W. Scott, and its value for recording fast separations illustrated by several traces showing separations carried out in less than 1 min.

The next section, "Theory and Application", was introduced by M. J. E. Golay, who discussed the relative importance of resistance to mass transfer in the liquid and gas phases with packed and capillary columns. He described how it should be possible to obtain lower height equivalent to a theoretical plate values by increasing the surface area of capillary columns without increasing the distance across which the solute molecules have to diffuse. This could be achieved by covering the inner wall of a capillary column with a finely divided clay before coating, and the improvement was demonstrated by showing a peak obtained for benzene before and after treating a column in this manner.

Capillary columns were the subject of the first two papers in this section, and investigations of the important operating and design features for achieving high efficiencies and high speed of analysis were reported by R. P. W. Scott and A. Goldup. Both discussed the effect of column diameter, film thickness and carrier gas on the height equivalent to a theoretical plate linear gas velocity curve and compared experimental results with those predicted by the Golay theory. R. P. W. Scott was able, by using carrier gases of different diffusivities, to show experimentally that, in accord with theory, the contribution from resistance to mass transfer in the gas phase to the total height equivalent to a theoretical plate was greater than that due to mass transfer in the liquid phase for solutes that are well retained. In general, a fair agreement between theory and experiment was found at gas velocities corresponding to the minimum height-equivalent to a theoretical plate, but at higher velocities the agreement was less satisfactory. M. A. Khan suggested that this may be due to the absence in the Golay equation of a term accounting for interfacial resistance between the gas and liquid phases, and reported that he had recently published a note¹ discussing this effect.

Examples of the efficiency and speeds of analysis achieved on capillary columns were reported by A. Goldup. Using a 600-ft. glass column, an efficiency of 300,000 plates had been obtained for a well-retained solute, and the separation of sixteen out of a blend of seventeen octane isomers was given as an illustration of the resolution attainable. The potentialities of capillary columns for high-speed analysis were demonstrated by chromatograms obtained using a recording system having a time constant of only a few milliseconds, which showed the separation of a blend of nine heptane isomers in 58 sec. and a simple four-component blend in 1 sec. C. P. Quinn presented equations derived theoretically defining the best conditions to achieve the minimum time of analysis and supported these with experimental data. The basic premise of using linear gas velocities

higher than the optimum was criticized by J. H. Knox.

In the first of the two remaining papers of the morning session S. J. Hawkes discussed factors which limit the maximum operating temperature of stationary phases. Valuable data on several stationary phases were given, and in addition the use of substituted borazoles at high temperatures was suggested.

Structural analysis of hydrocarbons by capillary gas chromatography in connexion with the methylene insertion reaction was the subject of a paper presented by M. C. Simmons. The author described how by simply treating paraffin hydrocarbons with diazomethane under ultra-violet irradiation a mixture of homologues of one higher carbon number could be obtained, and illustrated the value of this for obtaining retention volume data on inaccessible hydrocarbons. For example, retention volume results had been obtained for nineteen branched nonanes from six readily available octanes. One particularly interesting separation reported by the author was that of the diastereoisomers of 2,3,4-trimethylhexane. In the discussion that followed, J. F. Smith described the separation of an alcohol and a sulphide into *meso*- and *dl*-forms by gas chromatography.

Progress on large-scale preparative columns was also reported at the symposium. F. H. Huytens described how the loss in efficiency observed with preparative columns of large diameter could be attributed mainly to column packing. By carefully filling columns so that radial diffusion is large and axial diffusion small, height equivalent to a theoretical plate value of 2 mm. could be obtained with 3-in. diameter columns capable of handling samples up to 1 gm. The use of preparative scale chromatography for examining complex organic materials was reported by T. Johns.

Details of an apparatus for obtaining accurate retention volume data were given in a paper presented by E. R. Adlard. Specific retention volumes for cyclohexane and benzene on dinonylphthalate at temperatures from 48° to 110° C. were used to determine excess partial molar thermodynamic functions. For both systems investigated the excess partial molar entropies were found to be the predominant cause of the departure from ideality. In an interesting contribution to the discussion, J. C. Winters described some results obtained by R. L. Martin in which marked changes in the specific retention volume for hydrocarbons on polar stationary phases had been observed. To account for this, R. L. Martin had suggested that adsorption of the solute on the surface of the stationary phase contributes to the retention of the solute as well as solution in the stationary phase, and had shown that the former becomes of increasing importance as the percentage of stationary phase decreases.

The final papers presented in the section "Theory and Application" were by C. G. S. Phillips and his co-workers. They described the use of transition metal complexes and saturated solutions containing free undissolved tri-*o*-thymotide as stationary phases. The latter compound is of particular interest since it forms inclusion compounds with molecules of restricted width. By comparing retention data obtained for tri-*o*-thymotide with that for di-*o*-thymotide which does not form such complexes it was shown that the former selectively retards straight-chain compounds. The application of complexes of this type to give a separation according to molecular shape appears to be a most promising extension of gas chromatography.

The final day, devoted to "General Applications" of gas chromatography, was introduced by A. I. M. Keulemans, who described some of the results, using chromothermography, obtained by Prof. A. A. Zhoukhovitsky in the U.S.S.R.. By passing a ring furnace along the column during elution of the components it is possible to obtain symmetrical peaks using gas-solid chromatography at high sample concentrations. The technique enables samples of wide boiling-range to be examined, and has the added advantage that the temperature gradient and speed of the furnace offer additional parameters for controlling the separation.

The morning session was concerned mainly with the gas chromatography of inorganic compounds. Following a paper by G. Freiser describing the separation of the volatile chlorides of tin, titanium, niobium and tantalum at 200° C. on a 'Chromosorb' column coated with squalane, A. I. M. Keulemans mentioned that he had also separated volatile metal chlorides on an aluminium chloride-coated carbon column at temperatures up to 350° C. Both W. W. Brandt and J. Janak reported separating metals in the form of their acetylacetonates.

The chromatography of corrosive inorganic halogen compounds was the subject of two papers. T. R. Phillips employed a polytetrafluoroethylene capillary column coated with 'Kel-F' oils to separate mixtures of hydrogen fluoride, chlorine and chlorine trifluoride. A hydrogen-flame ionization detector, in which a platinum ring was maintained at red heat in the lower edge of the flame, was found suitable for detecting such inorganic compounds. Details of an apparatus incorporating a katharometer and automatic sampling valve, developed over a number of years for the analysis of plant streams containing highly reactive inorganic halide vapours, were given in a paper by G. Iveson.

Many other new and interesting applications of gas chromatography were described. J. Tranchant gave some results on the use of gas-solid chromatography

for the qualitative and quantitative analysis of mixtures containing nitrogen oxides, and D. W. Hill described the application of gas chromatography to anaesthetic research. An illustration of how detailed information on gasolines may be obtained by a combination of liquid-solid and gas-liquid chromatography was illustrated by a number of chromatograms in a paper presented by S. T. Griffiths. C. G. Scott gave details of a method for investigating the stability of white oils. The oxidation products of low molecular weight are eluted with a stream of nitrogen, condensed in special traps and examined chromatographically.

In a discussion in which retention volume data were mentioned, J. F. Smith outlined a useful practical method for expressing all retention volume data relative to one standard 'theoretical' nonane.

In connexion with work on compounds of high molecular weight, J. Janak described how the composition of non-volatile materials could be investigated by the gas-chromatographic analysis of their pyrolytic products. The use of esters as high-temperature polar stationary phases for examining products encountered in polymer production was discussed by R. E. Roland-Jones, and two materials, polyethylene glycol adipate and ethylene glycol distearate, were found suitable for use at 250° C. C. G. Scott stated that he had been able to elute hydrocarbons containing up to fifty carbon atoms using alumina modified by treatment with alkali metal hydroxides as the column packing.

In the final paper of the meeting, G. R. Boreham described an apparatus suitable for fuel-gas analysis, which had as a special feature a multicell thermal conductivity cell that enables four columns to be operated in series with a detector at the outlet of each.

The meeting ended with an excellent summing up of the symposium by C. S. G. Phillips and a closing address by R. C. Chirnside, president of the Society for Analytical Chemistry.

A. GOLDUP

¹ Khan, M. A., *Nature*, **186**, 800 (1960).

ION EXCHANGE

ON December 2, the Permutit Co., Ltd., demonstrated a new film entitled "An Introduction to Ion Exchange". The programme was introduced by Mr. Walters, who gave a brief outline of the development and uses of ion exchange procedures, mentioning in particular the preparation of acid-resistant anion exchange resins. The film, which is in colour, commences by illustrating some of the uses of ion-exchange resins, including the production of potable water from sea water. On the molecular scale, the structure of polystyrene-based cation and anion exchangers is demonstrated using conventional atomic models, with the exchange process simply illustrated. On the macroscopic scale, the hydrophilic nature of dehydrated resin beads is shown by wetting them, followed by observation of the resultant swelling.

The three main operations of ion-exchange are then examined: (a) *Separation*. Here two coloured organic ions in solution are allowed to flow through a resin column. While the blue concentrates in a narrow band near the top of the column, the red is less strongly held, forming a wider band which could

be eluted. (b) *Substitution*. The effect of passing a solution of potassium permanganate through a resin column in the chromate form is shown by a change in the colour of the solution from purple to yellow. (c) *Removal*. In this case a solution of a salt with two coloured ions, copper dichromate, is allowed to flow through a mixed-bed exchanger, resulting in the production of colourless 'de-ionized' water.

The exchange process is followed in more detail by a combination of demonstrations using copper dichromate and animated diagrams of sections through a resin bead in a flowing solution. A final survey of industrial aspects of water treatment completes the film.

Colour cinematography is an ideal medium for showing ion-exchange experiments, and in this sense the film is entirely successful. Nevertheless, although an attempt is made to discuss the mechanism of ion-exchange, a more critical and scientific approach would have been desirable. In particular, specific examples, in which the equilibria involved were considered in terms of quantitative data, would