H. Altmann (Reactor Centre, Siebersdorf, Austria) reported investigations using nucleic acids of tobacco mosaic virus to study the possible relation between trace-element levels and virus infection.

R. C. Koch (Nuclear Science and Engineering Corporation, Pittsburgh) described work on the distribution of iodine-129, a nuclide which occurs naturally as a result of cosmic-ray reactions and spontaneous fission, but has recently been found in measurable quantities in debris from nuclear explosions. The amount of iodine-129 in a typical human thyroid gland at the present time is about 10^{-11} g, and is far below the limit of chemical detection. Activation analysis, using thermal neutrons to produce iodine-130 (half-life 12.5 h), enables reasonably accurate measurements to be made, as a basis for the assessment of long-term biological hazards and for studies of the movement of iodine in the biosphere.

H. J. M. Bowen (Wantage Research Laboratory, U.K. Atomic Energy Authority) emphasized the wide discrepancies among different laboratories in determinations of certain trace elements in biological material. Experience in geochemistry and metallurgy has shown the value of standard samples, distributed for comparison of analytical results and techniques. Bowen suggested that several biological materials, including algae, cabbage leaves, locusts, muscle, bone and blood, should be grown or

collected under controlled conditions. About 100 kg of each material would be required for use over a period of 10–15 years. The samples should be dried, ground and distributed as required to laboratories working on activation analysis, so that they might compare their results on substantially identical specimens.

The main conclusion which emerged from the Colloquium is that activation analysis, having passed through the stage of being an ingenious technique, now constitutes a powerful experimental weapon for biologists, biochemists and clinical research workers. These beneficiaries have perhaps not appreciated fully the potentialities of new methods, but there is little doubt that the abounding enthusiasm of the effort now being applied to activation analysis will before long have a corresponding impact on biological science—including agriculture and veterinary medicine, which were not represented at all during this meeting.

Some of the participants were unprepared for the 12-h working day prescribed by the organizers. The arduous of this régime were handsomely mitigated by efficiency and hospitality, which culminated in a valedictory banquet at the château of Gif-Sur-Yvette under the genial chairmanship of Prof. Francis Perrin, high commissioner for Atomic Energy.

J. M. A. LENIHAN

GAS CHROMATOGRAPHY

AN informal symposium of the Gas Chromatography Discussion Group of the Institute of Petroleum was held at the Washington Singer Laboratories of the University of Exeter on September 27.

The first paper was given by Dr. I. Halasz on "Gas-Solid and Gas Adsorption Layer Chromatography". He pointed out that gas-solid chromatography has now become an important subject for research again after having been displaced for a period by gas-liquid chromatography. The disadvantages of gas-solid chromatography are: (1) the upper limit of linearity of the isotherms of gas absorption is normally higher than it is for the solubility of gases in liquids, and (2) the number of available solids with suitable mechanical properties is strictly limited. These disadvantages have now been largely overcome with the development of more sensitive detectors and new techniques. Among the latter, Dr. Halasz mentioned the modification of the highly polar known adsorbents by adding other solid substances, the coating of active solids with liquids for which Cremer has proposed the name 'gas adsorption layer chromatography', the coating of supports having a very large specific surface area with pulverized solids, and the coating of the inner wall of capillaries with a thin porous layer of solid. In the latter case, the whole of organic and inorganic chemistry is available for experiment. As regards the coating of an active solid with a liquid, preferably a polar one, some people assert that the active areas of the solid are blocked, and others suggest that the liquid changes its properties in the field of force of the solid, but Dr. Halasz was of the opinion that a new stationary phase is formed, and he showed a graph in which an increase in the amount of liquid coating of alumina caused a decrease in retention volume of all C_1 – C_4 components, a result in direct contrast to that obtained by gas-liquid chromatography.

Two of the main advantages of gas-solid chromatography and gas adsorption layer chromatography are that mass transfer is much faster than in gas-liquid chromatography, and also that the vapour pressures of the stationary phases may be neglected or are, at the least, very low, a factor of special importance in programmed temperature operation. Mass transfer will be especially fast in the case of a coating in the form of a thin porous layer, an advantage

previously pointed out by both Golay and Purnell. Five types of column were briefly defined as: (a) classical packed columns in which the inner diameter of the column is larger than the particle size of the support by at least a factor of 10; (b) packed capillary columns having an inner diameter less than 1 mm, the particle size of the support being larger than one-fifth the inner diameter of the column; (c) classical open-tubes or capillaries (Golay columns) which have the inner surface coated with liquid; (d) porous layer capillary columns in which the inner surface is coated with a thin porous layer of active or inactive solid; (e) porous layer bead columns in which glass or metal beads are coated with a thin porous layer of solid support. The performance of these types of column was illustrated by slides of work carried out by Heine and Horvath at Frankfurt. C_1 – C_4 hydrocarbons are separated fairly well on a packed capillary column of alumina in 13 sec, but although the resolution is a little better, separation took 360 sec on a classical packed column under the same conditions. It has been found that hydrocarbons up to C_8 can be analysed on these packed capillary columns using alumina without much tailing of peaks, but the column temperature must be relatively high (80° C). The same analysis can be carried out at 20° C by coating the alumina with 20 per cent by weight of β , β' -oxydipropionitrile. Many other similar illustrations were given, and in addition some separations using porous layer capillary columns of graphitized carbon black and silicon carbide, and porous layer glass bead columns using porous layers of zirconium oxide + triethylene glycol (for halogenated hydrocarbons) and ferric oxide + triethylene glycol (for aromatic hydrocarbons). In conclusion, Dr. Halasz emphasized that his research programme was still in its early stages, and it was hoped that, in the future, better adsorbents would become available.

A paper on "Modified Aluminas—A Progress Report" by C. S. G. Phillips and C. G. Scott followed and was read by Mr. Scott. The selectivity obtainable with aluminas modified with either sodium hydroxide or a sodium halide was briefly reviewed, and it was shown that, apart from providing packings having a range of aromatic/alkene retention ratios, they could also be used to separate

alkene *cis-trans* isomers. When aluminas are modified with cuprous chloride or silver nitrate, alkenes and aromatics can be held back completely, and the use of one of these packings as a subtractor was illustrated by two chromatograms of a Fischer-Tropsch Kogasin fraction. The first chromatogram, obtained on a sodium hydroxide modified alumina, gave all the alkane plus alkene peaks, and the second chromatogram, obtained on the same column to which a few millimetres' depth of cuprous chloride modified material had been added, gave the alkane peaks only. Apart from simple subtractor application in elution chromatography, the cuprous chloride and silver nitrate modified aluminas have been used to concentrate traces of alkenes and aromatics from large liquid volumes of alkane solvent. Recovery of the concentrates is achieved using gas-solid displacement chromatography. The main points to be observed with this procedure are: (a) the displacer vapour should be more strongly adsorbed than the component to be displaced, and (b) the displacement fronts should be sharp—this requirement being met if the column packing is retained in the column by a flat sinter disk. When the total mass of concentrate is much less than 1 mg, it is found preferable to trap out the displacer front containing the displaced material and to re-inject it on to a gas-liquid elution column fitted with an ionization detector. The recovery of μg amounts of 1-hexene and 1- and 2-heptenes from 100 g of *n*-heptane using this procedure with 1-octene as displacer was described (see *Nature*, 199, 66; 1963). The same technique has been used successfully to recover traces of lower alcohols and ketones concentrated on sodium bromide modified material using *n*-butanol as displacer. With esters, hydrolysis occurs and the recovered material is a mixture of ester and alcohol.

Aldehydes polymerized on the column and traces cannot be recovered. The strong interaction between the adsorbates and the modified aluminas is such that appreciable amounts of adsorbate can be held on the surface with a negligible concentration in the gas phase. Thus as much as 20 mg of heptenes can be retained at 75° C on 1 g of alumina modified with silver nitrate. A column containing 50 g of packing can, therefore, hold 1 g of heptenes for displacement, and the technique can be used for preparing pure materials at this level of sample size. The specificity of the gas-solid elution columns for *cis-trans* isomers is found to be present in the strong interactions on the silver modified material, and a 1.5 ml. charge of mixed 3-heptene isomers is separated into *cis*- and *trans*-fractions by displacement with 1-octene. In each case the fractions are recovered at better than 99 per cent purity. In order to obtain sharp displacement fronts, a sectional column is used having a 13 cm $\times$ 2 cm top section, a 10 cm $\times$ 1 cm centre section, and a 13 cm $\times$ 4 mm bottom section, in each of which the packing is retained by a sinter disk. High surface area solids such as carbon and silica-gel have also been used for preparative scale separations. The same apparatus holding 20 g of carbon is used to prepare ethyl propionate of better than 99.9 per cent purity. In the large-scale separation of ester mixtures and of hydrocarbon mixtures, it is found that at the change-over between pure components there is a high concentration of impurities together with a mixture of the two components flanking the change-over, and therefore the large-scale columns can be used either for the preparation of high-purity components or for the concentration of trace impurities.

"The Analysis of Surface Coating Resins by Pyrolysis-Gas Chromatography" was the subject of a paper read by Mrs. S. M. Rybicka, who emphasized the need for workers in such fields to be thoroughly conversant with the techniques of both pyrolysis and gas chromatography. She was of the opinion that many workers in the latter do not know enough about thermal pyrolysis to carry out investigations on polymers in an efficient manner, and this can easily lead to erroneous conclusions. Polymers

can be divided into three main types, depending on the amount of hydrogen they contain: (a) those with a considerable amount; (b) those with a medium amount; (c) those with a small amount. These will give different products on pyrolysis. The thermal fission of polymers may also take place in three ways: (1) fission in the backbone of the chain which will give rise to free radicals which then become converted to stable compounds; (2) fission between the backbone and side groups, giving rise to double bonds in the chain; (3) highly cross-linked polymers, which give mainly carbonaceous material and a small amount of volatiles. The second method gives products which are ideally suited to analysis by gas chromatography, but analysis is more difficult in the third group. Pyrolysis may give some indication of the group to which a polymer belongs, but difficulties often arise when trying to discover what part the breakdown products play in the original polymer. The 'fingerprint' technique of German workers may lead to considerable errors if the full implications of the results are not properly understood. All results should be checked by infra-red spectroscopy, which in many cases will give all the information necessary without recourse to gas chromatography at all. The gas chromatographic technique should be properly used to give complete resolution of all the products obtained, and the pyrolysis should be carried out under carefully controlled conditions. The thermal stability of polymers may be investigated by pyrolysis at various temperatures. In summary, pyrolysis-gas chromatography can be a useful method of investigation, but it is best combined with infra-red spectroscopy or some other method in order to confirm the products obtained. Care must also be taken to ensure that, so far as possible, the products of reaction are stabilized before secondary reactions occur.

Dr. F. H. Pollard presented a paper on "Gas Chromatographic Studies of Compounds of Group IV A Elements", which detailed work carried out on the chromatography of organo-silicon, -germanium, -tin and -lead compounds. Most of the illustrative examples were from silicon chemistry, but many of the points made could have been quite easily taken from the chemistry of the tin compounds investigated. In the examination of such compounds, more specific problems occur than with the organic compounds of carbon itself, so that a general review of the factors likely to be involved is of interest. The injection of the sample may follow the standard procedure, but if it is readily hydrolysed, oxidized, or spontaneously inflammable, then special precautions must be taken. 'Celite' or 'Silocel' column supports often need acid-washing treatment, and complete removal of the acid is very important, especially in the analysis of chloro compounds. The stationary phase must obviously be inert to the compounds being analysed. In general, silicone oils or hydrocarbons like squalane or 'Apiezon' can be used. Other phases useful for specific purposes are: (a) dinonyl phthalate; (b) tritolyl phosphate; (c) 60 : 20 : 100 diethyl phthalate : silicone oil E301 : 'Celite'; (d) silicone oil with a polypropylene glycol 400 plug; (e) 'Celite' having $n\text{C}_{18}\text{H}_{35}$ -groups bonded directly to it; (f) nitronaphthalenes, which are particularly useful for lower chlorosilanes. As detectors, the katharometer, flame ionization gauge and gas density balance have proved to be the most useful. With the katharometer, there is a successive increase in molar response for the tetraalkyls of silicon, germanium, tin and lead, and also much less trouble than anticipated has been experienced owing to reactivity of compounds on the hot wire. The best design of flame-ionization gauge is one in which the plates are vertical. It has a high sensitivity and calls for very small samples, especially in cases such as tetramethyl tin, trimethyl ethyl silane, and similar germanium, tin and lead compounds, where a saturation effect begins at a very low level. This effect is thought to be due to actual ionization characteristics in the flame. The gas density balance has been found to be almost universal in its application since

the corrosive gases encountered so frequently in work of this type do not come into contact with the electrical parts. It is found, however, that using such heavy molecular weight compounds of low boiling point, linearity is not observed except at very low concentrations—an effect illustrative of the kind of difficulty which may be encountered with work on unusual compounds. The gas density balance has also been used for phosphorous chlorides, lower members of the phosphonitrilic chloride series and for a range of phosphonitrilic fluorides. The problems met in the gas chromatography of organo-metallic compounds are well illustrated by the work described. The compounds were chosen carefully so that they were amenable to study in this way, coupled with other physical methods such as infra-red spectroscopy. Not only has gas-liquid chromatography enabled the analytical separation of materials to be carried out, but there have also been points of correlation between chromatographic behaviour and structure. Dr. Pollard emphasized the importance of gas-liquid chromatography in work of this kind, and advocated a bench-type chromatograph for every worker as standard equipment. The application of gas-liquid chromatography to the groups investigated was well illustrated by slides. In the case of the trimethyl silyl ethers, which hydrolyse easily and are thermally unstable on a katharometer wire, a maximum detector temperature of 150° C was used to preclude thermal breakdown, and the nitrogen carrier gas was carefully dried. Although polyethylene glycol should be an ideal stationary phase for such a separation, the tendency to hydrolyse such compounds (which is virtually complete at 100° C) makes it necessary to use tritolyl phosphate or hydrocarbon phases which result in some loss of peak symmetry. The methyl chlorosilanes have a narrow boiling range, and become far more liable to hydrolysis as chlorine replaces methyl. The most satisfactory stationary phase is 60 : 20 : 100 diethyl phthalate : silicone oil E301 : 'Celite'. Preliminary pyrolysis and catalytic studies have been carried out on the methyl chlorosilanes and the trimethyl aryl silanes, and also work on rearrangement reactions involving interchange of alkyl groups using aluminium chloride as catalyst. In the latter work, the number of alkyl groups used is such that it is possible to obtain 70 different products, many of which are isomeric and have closely similar boiling points. Gas-liquid chromatography is virtually the only

effective analytical method for such mixtures, and in order to identify individual components, most of the 70 possible compounds have been synthesized and their retention volumes determined. Gas-liquid chromatography is also used for preparative work. In conclusion, Dr. Pollard paid tribute to similar work being carried out independently by the Oxford Group under Mr. C. S. G. Phillips, and was able to report the good relationship and co-operation which exist between the two Groups.

The last paper, on "Polymer Pyromania", by C. E. Roland Jones and G. E. J. Reynolds, was presented by Dr. Reynolds. He emphasized the widespread nature and application of polymers, and that pyrolysis combined with gas chromatography provided a useful method for analysis and investigation. He distinguished between pyrolysis, by which he meant complete degradation to fragments, and stoving, which is a partial pyrolysis useful in thermal degradation investigations. The advantages of the technique are its speed, simplicity and the use of small samples, but the interpretation of the results obtained is not always easy. Very little work has been done in the quantitative field, and stringent conditions are necessary in order to obtain reproducibility of results. Four criteria are necessary to ensure this: (a) pyrolysis must be rapid and complete, and optimum conditions must be secured in order to obtain this; (b) there should be a large heating area in relation to the sample, and the temperature rise should be as rapid as possible—the usual conditions used by Dr. Reynolds were 700° C in 3 sec; (c) the possibility of gaseous diffusion must be kept to a minimum; (d) condensation of the products must be avoided. Sample size is also very important, and various workers have used samples varying from 10 mg to 20 µg, depending on the type of sample and ease of pyrolysis. It would seem that a thin film of sample is the most desirable form for rapid pyrolysis, although other forms have been used. Gas chromatography for the identification of breakdown products should be supplemented by infra-red and ultra-violet analyses, and the products should be removed from the unit as quickly as possible to avoid secondary reactions taking place. Slides of the pyrolysis unit and chromatograms of the breakdown products of various polymers were shown. It was noted that the 'fingerprint' system mentioned by a previous speaker could, in some cases, be a useful means of identification.

C. E. H. KNAPMAN

ADVANCES IN PROGRAMMING AND NON-NUMERICAL ANALYSIS

A FEW years ago a digital computer was regarded simply as a device which could do difficult sums very fast—given the good offices of someone versed in the black arts. The magical intermediary, the programmer, translated one's problem at great length into a special form of gibberish, known as 'machine code'. The final programme typically bristled with flights of hair-raising ingenuity, acquired in years of struggle with acute shortage of machine time and storage space.

The situation is rapidly changing. The advent, first of 'autocodes', and more recently of advanced programming languages, makes it increasingly possible for the user to describe his problem in terms which come naturally to the human mind and to leave it to the machine to translate his description into its own terms. Secondly, the enormous increase in speed and storage of the new generation of machines largely liberates the user from cramping pre-occupations with time and space. Finally the joint impact of these two developments is not only enlarging the power and range of the discipline known as 'numerical analysis'—the art and science of doing difficult sums—but has also thrown open the new territory of non-numerical analysis. Here the problems do not present themselves in primarily

numerical form and demand an approach based mainly on logical rather than on numerical manipulations.

One of the ways in which the University of Oxford Computing Laboratory, under the directorship of Dr. L. Fox, has responded to these developments has been by organizing a summer school on the theme "Advances in Programming and Non-numerical analysis". The course, which occupied the two weeks August 26–September 6, consisted of a series of some thirty lectures contributed by a panel of ten speakers. In the first lectures, the general theme of the course was outlined by Prof. S. Gill (Manchester College of Technology and Ferranti, Ltd.) and the scope of the new non-numerical applications of computers was indicated. Some of these belong to areas dominated by the immediate practical need for automatic aids, such as machine translation or medical diagnosis. For others, such as the discovery of new mathematical proofs, immediate utility is negligible, but the long-term impact on human thought and life is impossible to calculate.

Theorem-proving was taken by one of the speakers, D. C. Cooper (Bloomsbury Computers, Ltd.), for detailed survey, ranging from 'heuristic' techniques as utilized by