GAS CHROMATOGRAPHY

AN informal symposium organized by the Gas Chromatography Discussion Group of the Institute of Petroleum was held on March 12, 1965, in the Edward Lumley Hall of the Royal College of Surgeons, Lincoln's Inn Fields, London, with Mr. D. H. Desty in the chair. The symposium, which was preceded by the annual general meeting of the group, opened with Dr. D. W. Hill formally welcoming the visitors on behalf of the Royal College and describing some of the applications of gas chromatography in his own field.

In the first paper, entitled "Temperature Control in Gas Chromatography", presented by Dr. H. V. Carter (Perkin Elmer, Ltd.), the desirability of good temperature control was stressed particularly in the case of thermal conductivity detectors where a change in temperature as small as 0·001° C produces visible base-line shifts. In his discussion on types of heating systems, Dr. Carter stated that when the main consideration is negligible temperature gradient at low cost, a vapour jacket is most suitable although it has the disadvantages that the temperature is affected by pressure (0·4° C mm^{-1}) and a change in level is not conveniently made. When very tight temperature control is essential direct electric heating using the column itself as the element is suitable particularly for temperature programming because there is no time lag. Although this system is probably the best available, the user is restricted in his choice of column since its resistance must lie between defined limits. Moreover, temperature gradients are difficult to control if the column has variable thickness, although this can be overcome by removing metal from the column or varying the insulation where necessary. Proportional, on–off and programmed systems were discussed and illustrated by reference to commercial instruments and this was followed by detailed evaluation of the air-bath. While temperature control is difficult and acceptably low-temperature gradients are only obtainable with very high air velocities there is very little restriction to the dimensions of the oven and access to the column is generally very good. A method of calculating temperature gradients was described and shown to give values slightly lower than those obtained in practice. Dr. Carter concluded his paper with a brief review of the methods used for sensing changes, and the merits of thermocouples, bimetal strips, thermistors and platinum resistance-thermometers were compared. Discussion of this paper evolved mainly around the geometry of systems and insulation problems, during which Dr. Carter discussed in some detail the properties of the platinum resistance thermometer and mention was made of the good oven control obtained by using a bimetallic strip as a transducer.

The second paper, on 'Errors in Integration in Gas Chromatography", by Mr. W. A. Wiseman of Gas Chromatography, Ltd., was given in his absence by Dr. A. B. Littlewood. Integration errors were divided into two classes, fundamental and instrumental. It was pointed out that the area (A) of a chromatographic peak can be measured by integrating the signal (E) due to the detector with respect to time:

$$E = k_0 + (k - k_1)y + k_2y^2 \quad (1)$$

$$A = k_0t + (k - k_1)x + k_2\int(dx/dt)dx \quad (2)$$

where x is a measure of the detector signal (for example, charge) and $y = dx/dt$ (for example, current).

The first and third terms of equation (2) are responsible for the sources of error in the method, the constant k_0 being responsible for those incurred due to incorrect setting of the base-line, and k_2 for those due to non-linearity of the detector control. The constant k_0 is a function of a/h, where a is the decrease in peak height h due to incorrect setting of the base-line: in order to obtain accurate results a/h must be only a few parts per thousand. Large errors, which increase with the width of the peak, are caused by a drifting baseline and together with the error caused by incorrect setting of the base-line represent the largest error found in integration. Errors due to non-linearity of the detector increase with increasing peak height as does the ratio of the height to the area. If accurately reproducible samples are injected into the system at differing output sensitivities using a mixture giving a number of different peak heights, the ratio of dissimilar peaks should be constant. Peaks showing up early in the analysis occur at maximum rate at which impulses appear leading to an inherent, but small, error in the analysis.

Dr. Littlewood then considered errors in instrumentation. Integration is initiated by the appearance of a peak and this may be registered either when (1) the base-line exceeds a certain minimum, or (2) the slope exceeds a certain minimum; in both cases, however, a slight error is introduced at the beginning and end of a peak. In general, slope initiation is better than base-line initiation but difficulty is encountered when studying wide shallow peaks and a mechanism combining both modes of initiation was suggested as worthy of consideration. When integration is applied to partially resolved peaks meaningful results can only be obtained when there is a deep valley between them. In the ensuing discussion references were made to the importance of the right rate of counting, that results were calculated and not measured directly for non-linear integrators, that normalizing techniques should be used for accurate evaluation of results and that electronic integrators eliminate many of the errors mentioned.

Mr. R. Gittins (W. G. Pye and Co., Ltd.) introduced his paper on "The Evaluation of Performance of Flame-Ionization Detectors" by commenting on the value of the development work carried out by instrument manufacturers. Because of the difficulties involved in sampling very small masses the performance of high-sensitivity detectors had been studied using a vapour dilution vessel containing the sample under investigation dissolved in a non-volatile liquid (compare Fowlis, I. A., and Scott, R. P. W., *J. Chromatog.*, **11**, 1; 1963). Detector response was found to be independent of air flow above 400 ml. min^{-1} (below this value linearity occurs over a narrow range of concentration due to incomplete combustion) and independent of applied voltage above 20 vol. (45 vol. used in practice). The hydrogen to carrier gas ratio was found to exhibit optimum values.

"Dual Channel Gas Chromatography" was the title of a paper presented by Mr. P. Jenkins (Wilkens Instrument and Research *A.G.*) in which, after a résumé of the useful combinations of gas chromatography and other techniques was given, the complementary nature of the electron capture and flame-ionization detectors was described and illustrated by examples obtained with an instrument incorporating both. By splitting a column effluent into two streams, one to feed each detector, simultaneous though different chromatograms could be obtained: thus a sample of butyl phenol gave one peak (butyl phenol) on the flame ionization trace and five other peaks (impurities) on the electron capture trace: a refinery stream gave propane and propene on the former and oxygen, carbonyl sulphide, carbon disulphide and carbon dioxide peaks on the latter. The electron capture detector is unpredictable in its response to chemical compounds and is probably not linear although under standard conditions the ratio of peak heights flame ionization to electron capture may be used as an aid to identification. Problems of instrumentation and design were discussed with particular reference to the choice of voltage for the electron capture detector and considerable

interest was shown in the ability of the detector to respond to oxides of nitrogen.

The final paper, "Abnormal Characteristics of the Ionization Cross-section Detector", was presented by Mr. P. F. Washbrooke (The M.E.L. Equipment Co., Ltd.). After discussing briefly the main characteristics and modes of operation of ionization detectors, Mr. Washbrooke reported fully on cross-section types and the behaviour with reference to (1) the selection of carrier gas, (2) flow rate of carrier gas, (3) temperature, (4) linearity of response, and (5) predictability of sensitivity. A micro cell had been constructed in which the electrode arrangement was a cascade system in which the tritium electrodes were off-set with respect to each other in such a manner that the effective radiation surface area was increased with very little increase in cell volume. Hydrogen and nitrogen had been found satisfactory as carrier gases: helium and argon, although they could be used, responded more readily to other ionization effects (for example, drift effects). Response variations due to voltage changes had been considered and in particular it was found that unless oxygen in nitrogen carrier gas was subjected to suitably high voltages it responded to an electron capture effect. Detector response was found to be dependent on the rate of mass input, independent of carrier gas flow rates between 10 and 100 ml. min^{-1} and independent of temperature up to the safe working limit of tritium (200° C). The linearity of response, which depends on energy losses in the primary radiation stages, is linear over many orders of magnitude for tritium as well as strontium-90 if the interelectrode path is small compared with that of a β-particle, and it is important to note that the detector can handle sample sizes considerably larger than any other type. Predictable relations have been obtained between peak area responses per millimole and values calculated from molecular cross-sections for *n*-paraffins, alcohols and monocarboxylic esters, but large deviations occur for aromatic hydrocarbons, aliphatic ketones and halogenated hydrocarbons. When quoting responses the radiation source should be given, as differences of up to 16 per cent are obtainable for cross-sections examined by different radiations. Changes in temperature may also affect the response characteristics. Mr. Washbrooke concluded his presentation by stating that the cross-section ionization detector is ideal for on-stream monitoring in preparative-scale gas chromatography when used with hydrogen or nitrogen carrier gas in order to minimize electron drift effects. The discussion was opened by Dr. H. Boer, who spoke of the anomalous behaviour of helium as carrier gas and mentioned his own version of a micro cross-section detector which had given excellent results for the detection of low boiling compounds. The remainder of the discussion was concerned with the use of the detector in the analysis of town's gas, the advantage of using argon as carrier when permanent gases were to be detected and the saturation of helium carrier gas with water to remove drift effects.

D. R. Browning

INTERNATIONAL ATOMIC ENERGY AGENCY

At its meeting in February, the Board of Governors of the International Atomic Energy Agency gave approval for the nearly one hundred projects of assistance by Agency experts and equipment in thirty-eight countries to be financed from Agency funds under the 1965 Programme. This is in addition to the work financed under the United Nations Expanded Programme of Technical Assistance. The number of requests for experts and equipment continues to increase, largely because several member states have now set up research reactors and established laboratories under bilateral arrangements. For 1965 the estimated cost of the provision of experts and equipment from Agency resources is 874,000 dollars, of which about one-third is for equipment and supplies. The work covers a wide range; about thirty projects deal with the production of radioisotopes and their application in medicine, agriculture, hydrology, food preservation and industry, and the remainder are concerned with reactors, health and safety, instrumentation, special branches of chemistry and physics, and the prospecting and processing of raw materials.

In Africa, the Congo is enlarging its research reactor and laboratories to form a regional centre and the Agency is providing an expert on nuclear electronics and a radiobiologist. Ghana is completing the construction of an experimental reactor at its nuclear research institute near Accra and will be assisted by a reactor programme specialist and a nuclear physicist. Morocco's geological service is to be helped by the introduction of geochronological methods, and Tunisia is to receive advice on aerial prospecting for nuclear raw materials. Senegal, Rhodesia and the United Arab Republic are to be given help on the use of radioisotopes.

Equipment consisting of a pulsed neutron source and a pulsed neutron logic unit, together with assistance in reactor physics, are to be given to Argentina, and in Chile a biophysicist will advise on the development of electron spin resonance and its applications. Bolivia, Brazil, Mexico, Peru and Uruguay are also to receive expert assistance and advice. In Europe and the Near East, Afghanistan, Greece, Iran, Israel, Lebanon, Portugal, Turkey and Yugoslavia will all be visited by various nuclear scientists. In South-east Asia and the Far East, Burma will be sent standard works on nuclear physics and engineering; Cambodia and Ceylon advice and equipment relating to the use of radioisotopes; the National University Hospital in Taiwan, China, advice on the use of its cobalt teletherapy unit; Thailand an entomologist and equipment to undertake the study of the use of radiation for the control of insect pests; and India, Pakistan, Hong Kong and Viet-Nam experts for agricultural and food preservation research and assistance in teaching programmes.

S. Weintroub

THE AMERICAN OYSTER

For some forty years Dr. Paul Galtsoff has served as shellfish biologist with what is now the U.S. Fish and Wildlife Service. Of recent years, while holding the post of senior scientist in that Service, he has been engaged on the production of a comprehensive account of the American oyster, *Crassostrea virginica*. He has had the initial benefit of the widest experience of both laboratory and field investigations, his work on reproduction in *C. virginica* is classical while, as he tells us, he has studied oysters and related bivalves off every coastal State in the United States, in the Hawaiian Islands, in the Gulf of Panama and on Margarita Island, Venezuela.