properties are particularly sensitive to the molecular weight distribution as well as to the average: for example a small fraction of very long molecules will markedly increase melt viscosity and a few short molecules can disproportionately reduce the breaking strength.

Separation in GPC is due to differential exclusion of the randomly coiled macromolecules from pores in the particles of the column packing. Larger molecules are excluded from more pores and flow faster through the column. In operation the technique is clumsy. High temperatures are needed to keep many polymers in solution and this temperature must be closely controlled along 3–4 foot columns. High pumping pressures are needed but pressure variations must be minimised. The column packing may be cross-linked porous polystyrene particles, which are difficult to pack and use, or porous glass particles, but adsorption effects make such glass packings unsuitable for polar polymers. The eluting polymer is usually detected by differential refractive index measurement. A typical run takes 2–3 hours and a change of the solvent system is a major operation. Ideally, calibration would be performed using narrow molecular weight distribution polymers under the same conditions as the subsequent runs, but only for polystyrene are such fractions readily available. This problem is avoided by use of a universal calibration curve based on the assumption of separation by molecular volume and on known viscosity-molecular weight relationships for the polymer under run conditions. This calibration has often been questioned—for instance Otsuka and Hellman in *J. Polymer Sci. (letters)* (12, 331; 1974), show that it is successful for polystyrene on glass bead columns in a range of solvents but not on polystyrene-bead columns where the pore size is probably also a function of solvent.

Thus GPC is at present suitable for application where a large number of similar samples are to be measured but lacks the flexibility or accuracy necessary for research applications and is too slow for on-line process control.

Two papers by Ouano and Ouano and Kaye describe progress in the development of a molecular weight, continuous flow detector which would eliminate the calibration problem. The first (*J. Polymer Sci. (A-1)*, 10, 2169; 1972) described the construction of a viscosity detector which measures the pressure drop in a capillary. Molecular weight could be determined to within 10% in a 10 μ l cell at concentrations of less than 10^{-1} g l $^{-1}$ and flow rates of 1 ml min $^{-1}$. The main drawback is the sensitivity to pump pulses.

A recent paper (*J. Polymer Sci.*

(Chemistry), 12, 1151; 1974) describes a low angle laser light scattering detector using a 6 μ l cell which will work at concentrations of 10^{-2} g l $^{-1}$, for molecular weights from 10^2 to 10^6 . Between the column and the cell a filter is necessary to remove fragments of column packing. The volume of the filter and its connecting tubing significantly reduces the resolution of the present system.

High speed GPC is a second recent development which is being studied in several laboratories. Unger *et al.* (*J. Chromat.*, 99, 435; 1974) describe a system using polystyrene gel particles in which a 2 foot long column of 5 μ m particles could separate a polystyrene sample in 10 min, at a flow rate of 2.5 ml min $^{-1}$. Ultimately high speed must be at the cost of resolution but the use of small particles offsets this.

Radioactive tracers in the atmosphere

from D. H. Peirson

THE use of fission product pairs with similar half-lives as meteorological tracers is described in a recent paper (Holloway *et al.*, *Journal of Geophysical Research*, 79, 4453; 1974). This is a recent example of the exploitation of radioactive tracers in the atmosphere, a technique that has developed considerably during the last twenty years.

The impetus came during the 1950s when it became necessary to determine the distribution of nuclear weapon debris by taking samples of airborne dust or rainwater and to attempt a quantitative estimate of the radioactivity in order to assess the radiological hazard. At first it was possible only to measure the gross radioactivity of the sample and then make corrections for decay, according to a crude assumption that the beta-radioactivity of the fission product mixture varied more or less inversely with time. Soon however the full sensitivity and resolution of the radioactive tracer method became available when samples of airborne dust and rainwater could be analysed for specific radionuclides.

The earliest and probably most rewarding achievement of this technique was the confirmation of the seasonal reinforcement of the troposphere in the early summer of each year by air from the stratosphere. The variation of the concentration of strontium-90 (half-life 28 year) in rainwater, and subsequently caesium-137 (30 year) in air, gave ample demonstration of the effect which had been previously indicated by the behaviour of ozone and water vapour in the atmosphere. At the same time it was possible to show that the radioactivity transferred from the stratosphere appeared in the troposphere with a maximum in mid-latitudes and minima at pole and equator.

The next advance in exploitation of the technique was to extract qualitative as well as quantitative information from these observations by measuring the radioactivity of

pairs of fission products. Thus the ratio of strontium-89 (50 day) to strontium-90, of cerium-144 (285 day) to caesium-137 and of various other combinations could be used to estimate the date of the fission explosion, or if the date was known then these ratios could indicate the proportion of nuclear debris released by the latest explosion against a background from earlier events.

Because the bulk of fission radioactivity has been inserted into the stratosphere it is possible to determine, by observations of these radioactive tracers, the delay of stratospheric residence time before the material returned to the surface of the Earth. The massive explosion series of 1961–62 were followed by several quiet years when it was possible to determine unambiguously a mean residence time in the (lower) stratosphere of about 16 months by measuring the decrement of the long-lived fission products strontium-90 and caesium-137. It was also possible to show, during this period when the northern hemisphere contained so much more fission radioactivity than the southern, that the mean residence time against interhemispheric transfer was between three and five years.

Meanwhile the radioactive tracer method has been used with natural radioactivity, derived both from the surface of the Earth and from cosmic radiation. Radon-222, emanating from terrestrial radium, has a succession of radioactive descendants, the longest-lived of which are lead-210 (22 year) and polonium-210 (140 day). These two tracers have been used, separately or relatively, as an index of the residence time in the troposphere, the resuspension of dust and the prevalence of continental or oceanic winds. A number of radioactive species are produced by the interaction of cosmic radiation with atmospheric nuclei. Of these, for example, the ratio of beryllium-7 (54 day) to phosphorus-32 (14 day) has been used to indicate vertical movements in the atmosphere.