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Note

Performance of an evaporative analyser detector for gel permeation chromatography

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This paper describes the performance of a new type of detector for gel permeation chromatography (GPC), developed from an earlier detector proposed for liquid chromatography, in relation to that of a differential refractometer. The comparison is reported in terms of a calculation of the number and weight average molecular weight of a commercial polystyrene sample and also in regard to the measurement of the complex molecular weight distribution of a mixture of epoxy resins.

EXPERIMENTAL

The Evaporative Analyser (EA) detector is made by Clanor Instruments (Balwyn, Australia) and consists of three stages; atomiser, evaporator and detector. It was originally designed by workers at Union Carbide (Sydney, Australia) as a detector for liquid chromatography especially suitable for use with mixed solvents¹. The particular features claimed were a steady baseline and good sensitivity for a wide range of compounds provided they were of significantly lower vapour pressure than the solvent. Further development of this detector was undertaken by Clanor Instruments, in association with workers at the University of Melbourne, who brought it to its present form. The arrangement is now as shown in Fig. 1. The sample column eluent passes through the atomising head. A primary air stream entering at the top of the detector column assists atomisation of the liquid by spraying it inside the heated evaporative column. The secondary air, which enters at the bottom of the evaporative column, flows upwards outside and downwards inside the heated column carrying the atomised solvent stream. As the solvent droplets pass down the heated column, the solvent evaporates and any non-volatile solutes present remain as a fine cloud of particles. The heated column consists of a fine mesh gauze: the secondary air thus to some extent enters the central region through this gauze, thereby assisting to prevent deposition of the atomised mist on the walls of the column. When this cloud of particles passes through the light path at the bottom of the column, the light scattered by the particles is detected by a photomultiplier located at an angle of 120° to the incident light beam. The signal from the photomultiplier is amplified and displayed on a recorder.

The EA detector response should be proportional to the amount of sample

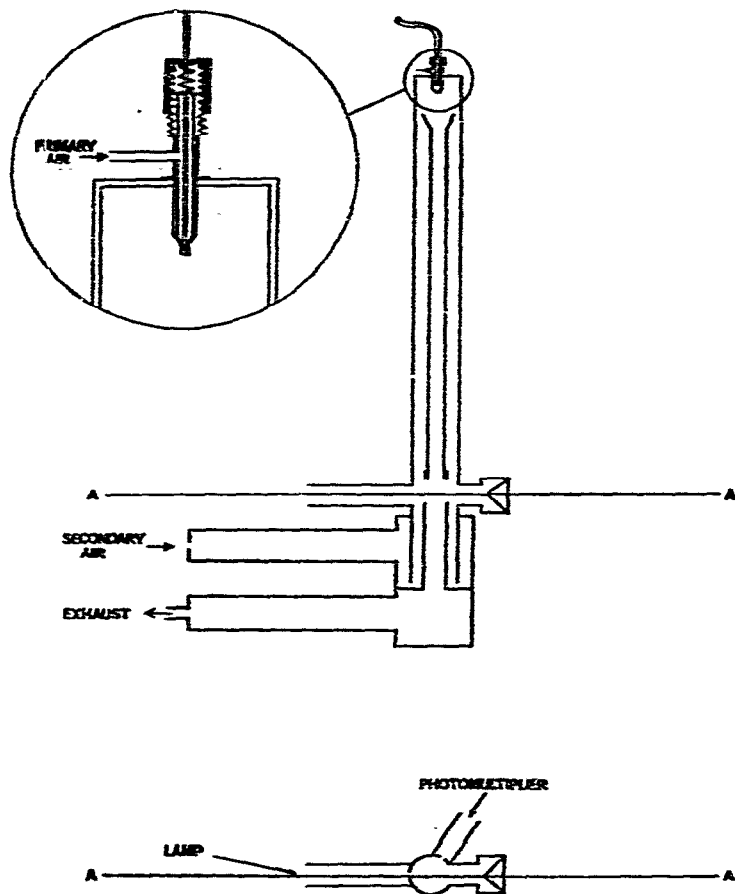


Fig. 1. Schematic diagram of EA detector.

present in the eluant providing that none is lost during the evaporation of the solvent, and that the particles are of a uniform size and shape.

The use of this detector for measurement of molecular-weight distribution of styrene-butadiene rubber samples has been described recently².

The performance of the EA detector in relation to that of a Varian model 02-1528-02 refractive index (RI) detector was studied using the two in parallel on a Clamor Instruments gel permeation chromatograph fitted with Styragel columns³.

Samples of polystyrene of narrow molecular weight (Pressure Chemical, Pittsburgh, Pa., U.S.A.) were used as calibration standards. A sample of Styron 685, a commercial polystyrene (Dow Chemical, Altona, Australia) was employed for determination of the number- and weight-average molecular weight from the two chromatograms. A mixture of three epoxy resins (the chloroform soluble part of an aircraft film adhesive) was also examined. The instrument was operated on analytical-reagent grade chloroform at 30°.

RESULTS AND DISCUSSION

Experiments associated with operating conditions showed³ that parameters such as the primary air pressure, the secondary air flow-rate and the lamp age affect the relationship between the EA detector response and the amount of solute injected. However, for a given set of operating conditions, the response was found to be proportional to the amount of solute to a first approximation. Solute volatility effects were discernible for molecular weights less than about $1 \cdot 10^5$. Chromatograms displayed good baseline stability and were insensitive to minor changes in solvent composition.

With the two detectors connected in parallel to the column EA and RI chromatograms were produced of a commercial polystyrene sample. A set of three columns was used (nominal porosities $1 \cdot 10^6$, $2.5 \cdot 10^4$ and $1 \cdot 10^3 \text{ \AA}$) and the detectors were adjusted to give chromatograms of approximately the same peak height and width. Following the method of Cazes⁴, the molecular-weight values shown in Table I were calculated. The reproducibility of the results was about 5%.

TABLE I

MOLECULAR WEIGHTS OF A POLYSTYRENE SAMPLE CALCULATED FROM RI AND EA DETECTOR CHROMATOGRAMS

Detector	$\bar{M}_w \times 10^{-5}$	$\bar{M}_n \times 10^{-5}$	\bar{M}_w/\bar{M}_n
RI	3.13	1.01	3.09
EA	2.91	0.96	3.04

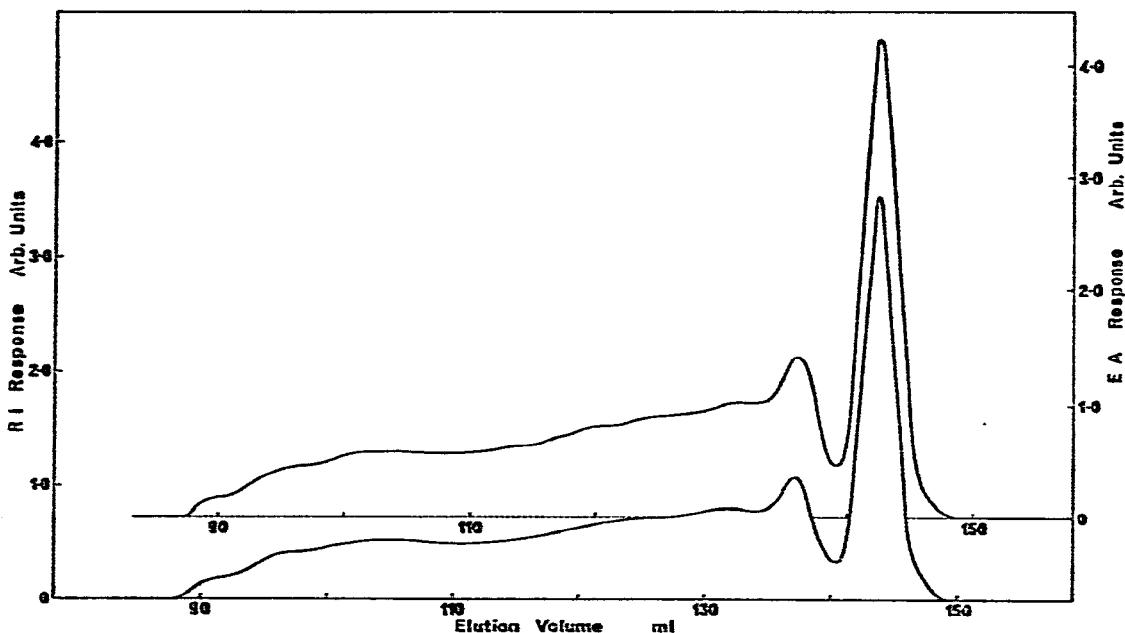


Fig. 2. EA and RI chromatogram of an epoxy-based film adhesive.

The arrangement of the two detectors in parallel was also used in a study of the chloroform extract from an aircraft adhesive. This material is a mixture of three epoxy types (and their oligomers), namely (a) a diglycidyl ether of bisphenol A of high molecular weight, (b) a cresol novolac, and (c) triglycidyl *p*-amino phenol⁵. The column set consisted of four columns of nominal porosities $3 \cdot 10^3$, $1 \cdot 10^3$, 500 and 200 Å. The chromatograms of this mixture are shown in Fig. 2.

It appears that the EA detector enables determinations to be made of molecular weight to about the same accuracy as the RI detector. Its baseline stability, overall reproducibility and insensitivity to minor solvent composition changes are distinct advantages. However, its dependence on various operating conditions are disadvantages, especially the dependence on lamp age. It is concluded that the EA detector is in principle a useful addition to the range of GPC detectors, but that the design is not yet the optimum.

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