

CHROM. 5553

## Use of an electron capture detector for monitoring in liquid chromatography

Liquid-phase chromatography has not had as wide a use as gas chromatography as an analytical technique because no detector of comparable sensitivity was available for it. Many authors have studied this problem in recent years and have proposed some solutions<sup>1-3</sup>.

In this paper a possible application of the electron capture detector<sup>4</sup> to liquid-phase chromatography will be described. Under the conditions described the detector exhibits the same selectivity and sensitivity as in gas-phase chromatography. For some years now, the moving wire detector developed by JAMES *et al.*<sup>5</sup> and SCOTT<sup>6</sup> employing both argon and flame ionization detection has been in use for monitoring liquid chromatographic columns. A further development of the moving wire detector has been accomplished in Cambridge by adapting the electron capture detector to monitor the eluent from liquid chromatograph columns. At the present time this system is manufactured commercially by the Pye Co., Cambridge<sup>7</sup> and obviously differs in many respects from that developed by us and described in the present paper.

### Experimental

The detecting system consists of two essential parts, *viz.* the nebulizer and the electron capture detector. The eluent coming from a chromatographic column is nebulized continuously and part of it is admitted into the interior of an electron capture detector, kept at an appropriate temperature to avoid condensation and adsorption. It was found necessary to limit the gas flow in the detector by a needle valve in order to obtain its best performance. The scheme of the apparatus is presented in Fig. 1.

Several trials have been performed with the apparatus with regard to both the eluents and the substances to be detected. For the eluents, it is vital that they have a low electron affinity; in other words, it is important that they do not suppress a large portion of the standing current. The following eluents have been tested: benzene, hexane, cyclohexane, pyridine, methanol, ethanol, ethyl ether, and acetone. Only the latter two reduce the standing current to some extent, but this did not prevent their use. The solvents were analytical grade (C. Erba, Milan), and were used without

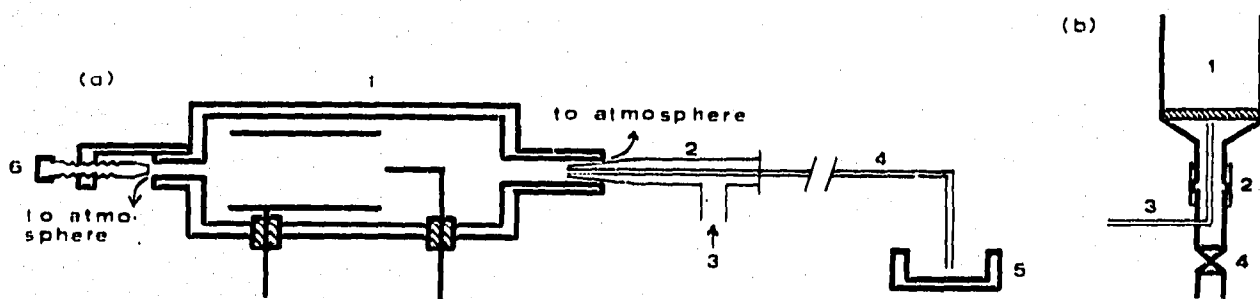


Fig. 1. (a) Schematic representation of the device; 1 = Electron capture detector, the heating system of which has been omitted for the sake of clarity; 2 = nebulizer; 3 = gas inlet; 4 = teflon capillary; 5 = sample reservoir; 6 = needle valve. (b) Chromatographic column-detector coupling system; 1 = Chromatographic column; 2 = silicon rubber joint; 3 = stainless steel capillary (0.18 mm I.D.), which inserts into the nebulizer teflon capillary; 4 = tap.

further purification. The detector used contained a tritium source and was manufactured by C. Erba, Milan.

The operating conditions are given in the legend to Fig. 2. The standing current was about  $5 \cdot 10^{-9}$  A and did not vary when the eluent was introduced, except in the case of ether and acetone. When used in this way, the detector had only a slightly larger noise level ( $2 \cdot 10^{-11}$  A) than when used in gas chromatography.

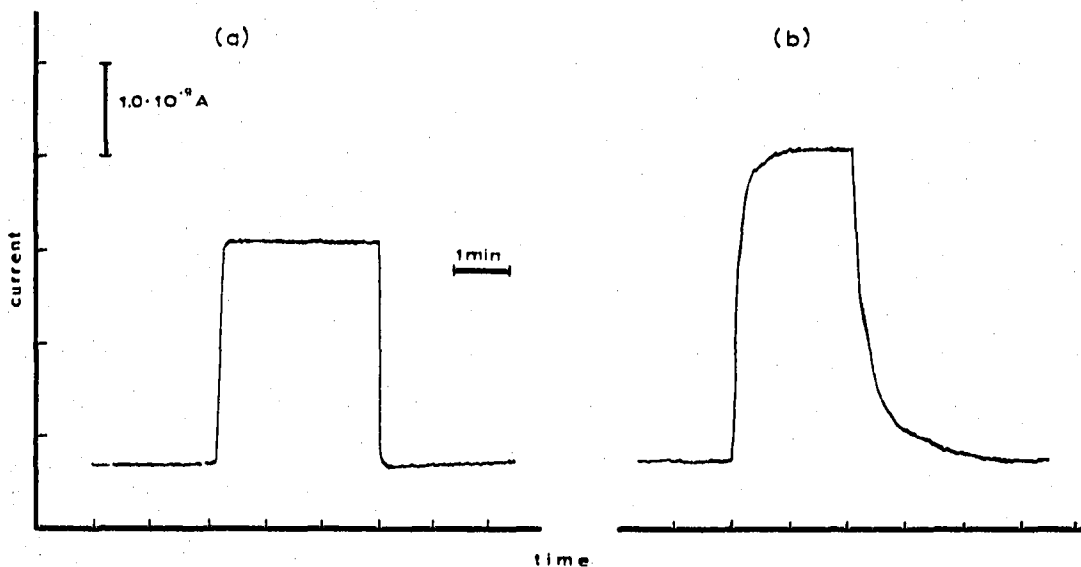


Fig. 2. Recorder response for (a) chromium tris(trifluoroacetyl)acetate and (b) *p*-nitrophenol. Nitrogen flow rate, 500 ml/min; liquid flow rate, 10  $\mu$ l/min; detector temperature, 150°; applied potential, 20 V.

It is noteworthy that the system permits the use of water as eluent, which leads to the conclusion that water does not have a high electron capturing ability. The possibility of using the detector with this solvent, which is widely employed for liquid-phase separation, considerably enhances the applicability of the system described, provided a  $^{63}\text{Ni}$  source is used. The experiment here was performed with water-ethanol (5:95), in order that damage to the tritium source, with which the apparatus is at present equipped, should not occur.

We first tested substances that are stable in the gas phase and whose behaviour in gas-liquid chromatography (GLC) is well characterized, *viz.* chloroform, tetrabromoethane, lindane, nitrobenzene, *p*-nitroanisole, chromium tris(trifluoroacetyl)acetate. The sensitivity of the detector towards these substances is similar to the sensitivity of the same detector used in the traditional manner. The sensitivity tests on the above-mentioned components were carried out by allowing solutions of the component at known concentration and pure solvent to flow alternately. In the case of column separations the adaptor illustrated in Fig. 1b can be used. The component is detected as a step with a low rising time and very good stability (Fig. 2a). The reproducibility is excellent. A typical standard curve for chromium tris(trifluoroacetyl)acetate is shown in Fig. 3.

In view of the interest of the results described above, we next studied the behaviour of substances of low volatility and/or heat sensitivity towards the described

system. For this purpose we selected 2,4-dinitrophenyllysine, *p*-nitrophenol, copper bisacetylacetonate, diethyl stilboestrol diphosphate. With this group of substances the detector appears equally sensitive, even though it showed some tailing effects, see Fig. 2b. This effect can be attenuated by raising the mean temperature of the detector and avoiding excessive cooling effects by the gas flow in the first part of the detector. The experimental verification of the last point has been limited to a temperature of 200°, which is the maximum working temperature for a tritium source. We plan to investigate this problem further using a <sup>63</sup>Ni source, which can operate up to a temperature of 400°.

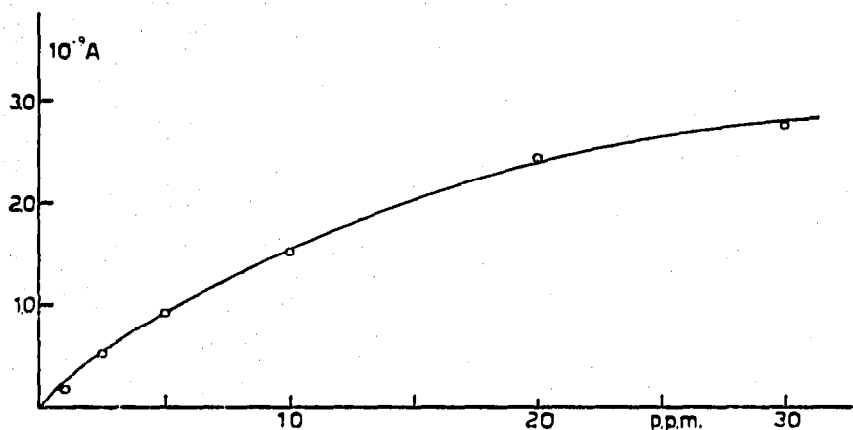


Fig. 3. Current-concentration plot for chromium tris(trifluoroacetylacetonate). The operating conditions are the same as those reported in the legend to Fig. 2.

### Conclusions

The system described above permits volatile substances with an electron affinity to be detected without difficulty in a liquid phase. Thermolabile and/or low vapour pressure substances can also be detected, but some tailing due to the system occurs. This effect can probably be made negligible by using an apparatus which is able to work at a temperature of about 400°. In this case the range of applicability of this system would be greatly extended.

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GIORGIO NOTA  
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