

Notes

CHROM. 3745

Electrodeless discharge as detector in gas chromatography.**IV. Comparison with a thermal conductivity detector**

The use of an electrodeless discharge as a detector in gas chromatography has been described earlier¹⁻³. It consists of two coaxial glass tubes sealed as in a Siemens' type ozonizer through the annulus of which pass the effluents from the gas-solid chromatographic (GSC) or gas-liquid chromatographic (GLC) column. The tube is excited in a low frequency electrodeless discharge at a constant potential and the discharge current, after rectification by a crystal, is measured by a galvanometer, or, a suitable potential drop of the output, after smoothening, is fed to a strip-chart recorder. The background current due to the carrier gas is conveniently brought to zero by a small bias potential and the noise level is satisfactorily reduced. The arrival of each gas or vapour sample into the detector from the column is marked by a signal of a sharp change of discharge current ($\pm \Delta i$) in the galvanometer, or as a peak on the recorder chart. The resolution time is short and no additional amplification is necessary for samples of the order of $0.1 \mu\text{mole}$. The signal strength for a given sample, measured as the area under the peak, is controlled by the dimensions of the detector (height, ratio of the diameters of the outer and inner tubes and the annular width), its temperature and the excitation voltage, conditions in regard to the column and the carrier gas being constant. It is easy to find a range of conditions for each GSC or GLC and sample system over which the signal height is linearly related to the quantity of the substance present in the sample injected.

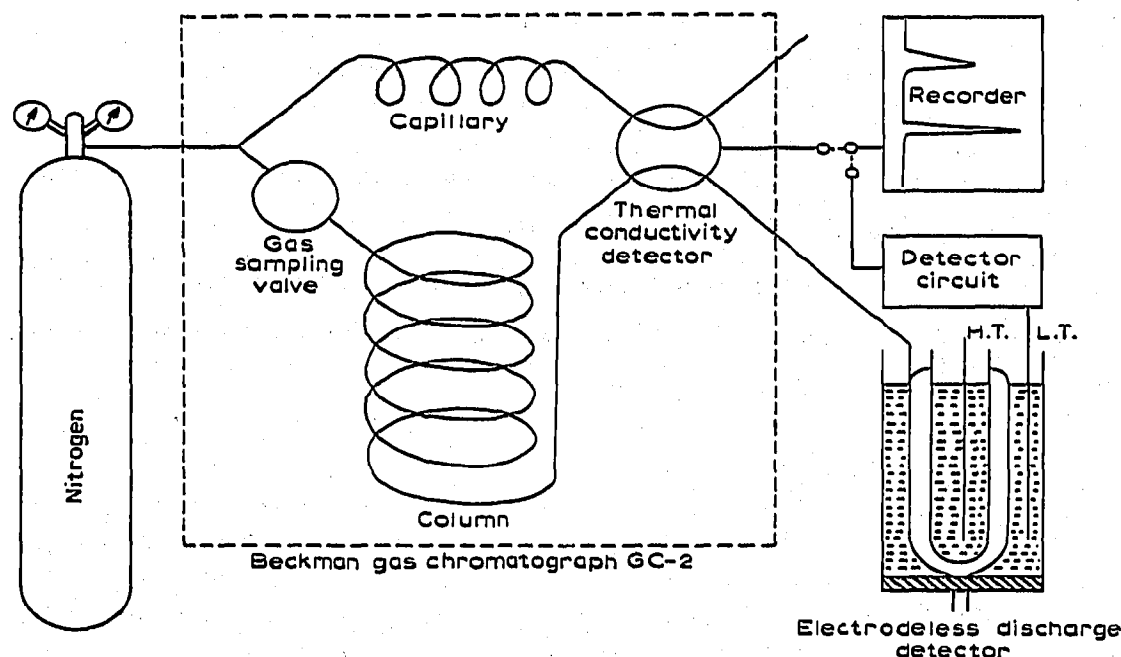


Fig. 1. Schematic diagram of the experimental set up.

Details of the construction and working of the new detector and the results of the separation of a number of inorganic and organic gases and vapours and the factors controlling the detector sensitivity have been published earlier¹⁻³. In the present note a comparison has been made between the efficiency of the detector and that of a thermal conductivity detector commonly used in a commercial instrument.

Experimental

In the present work the signals obtained with the electrodeless discharge

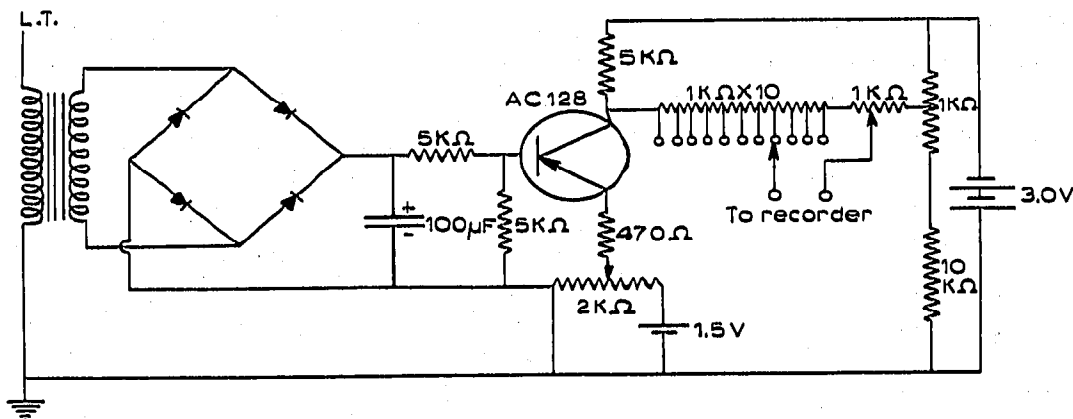


Fig. 2. The detector circuit.

detector for a variety of gases and vapours have been compared with those from the thermal conductivity detector (filament type) of the Beckman gas chromatograph

TABLE I

COMPARISON OF SIGNALS WITH THE THERMAL CONDUCTIVITY DETECTOR AND THE ELECTRODELESS DISCHARGE DETECTOR CONNECTED IN SERIES FOR VARIOUS SUBSTANCES

Carrier gas: nitrogen; column inlet pressure: 2 kg/cm²; column: silicone oil (20%) supported on 40-60 mesh firebrick powder; length, 1.8 m; temperature, 70°. The signal is expressed in number of divisions of the recorder chart paper.

Series No.	Substance	Signal (peak height)	
		(A) Thermal conductivity detector	(B) Electrodeless discharge detector*
1	Oxygen	12	> 100
2	Carbon dioxide	20	103
3	Chloroform	7	100
4	Carbon tetrachloride	4	88
5	Acetone	8	> 100
6	Ethyl methyl ketone	3	48
7	Methyl acetate	3	40
8	Ethyl acetate	6	100
9	'Burshane' (domestic fuel gas, mainly butane)	3 peaks: 1.0, 1.5, 3.5	5 peaks: 78, >100, 85, 36, 22

* Here only a fraction of the signal obtained was fed to the recorder so as to be within the maximum limit of the recorder chart.

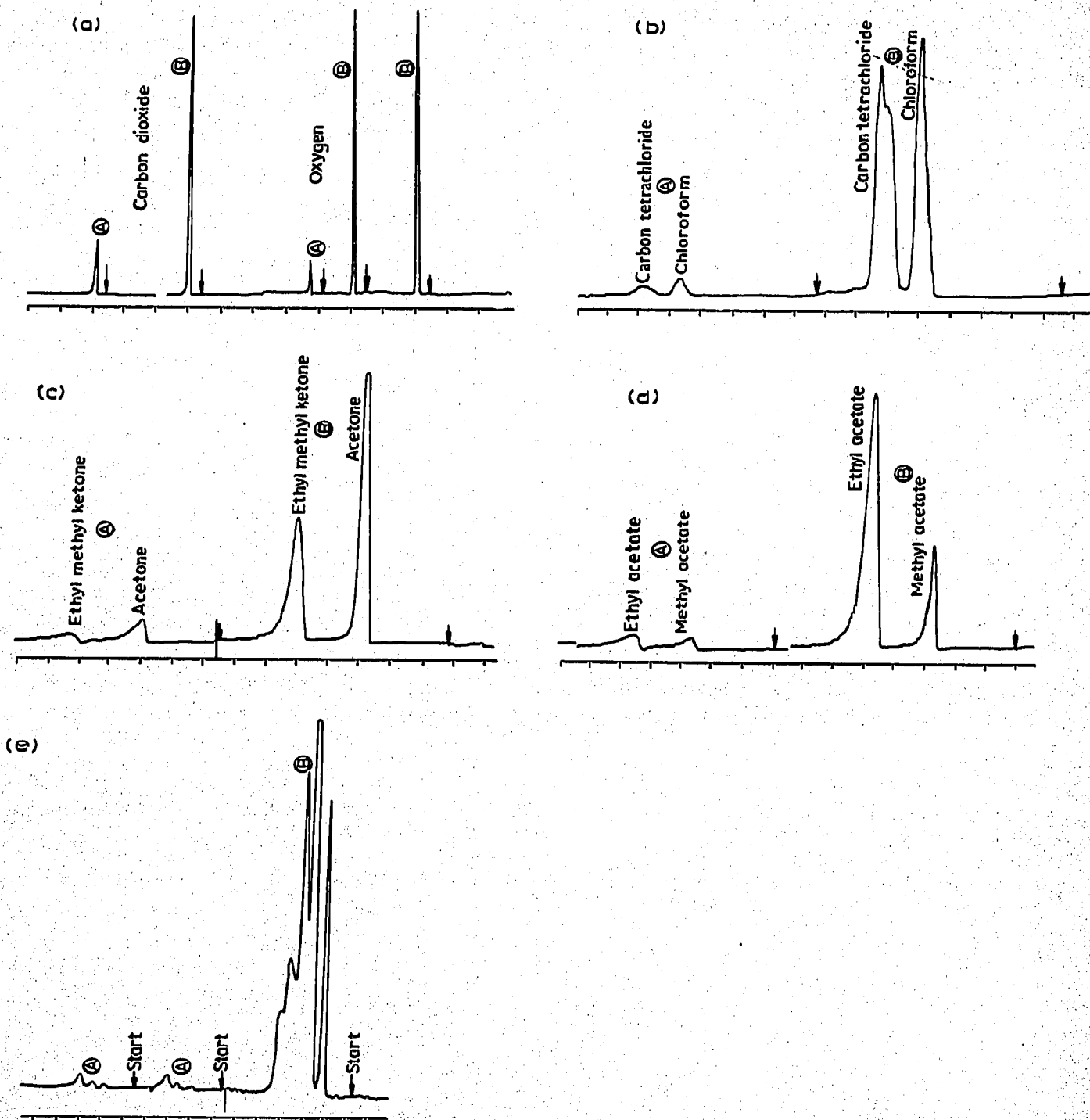


Fig. 3. Comparison of signals with (A) the thermal conductivity detector and (B) the electrodeless discharge detector for various systems: (a) oxygen, carbon dioxide; (b) mixture of chloroform and carbon tetrachloride; (c) mixture of acetone and methyl ethyl ketone; (d) mixture of methyl acetate and ethyl acetate; and (e) domestic fuel gas 'Burshane', mainly butane. Carrier gas: nitrogen.

GC-2. The new detector is connected at the exit of the Beckman gas chromatograph, so that the two detectors (the thermal conductivity and the electrodeless discharge) are in series and are operated simultaneously under identical conditions; the carrier

gas, column, gas sampling valve and injection system for liquids, being common to both. The output of either detector can be fed to the strip-chart recorder (Bristol's Dynamaster Recorder, 1 mV for full-scale deflection). Fig. 1 is a schematic diagram of the experimental set up and Fig. 2 gives the circuit diagram used in conjunction with the new detector. The chromatograms for 5 different systems recorded by the two detectors are shown in Fig. 3 and the corresponding peak heights in Table I.

Results and discussion

Fig. 3 and the results summarized in Table I clearly show that under the same operating conditions the signals from the electrodeless discharge detector are much stronger than those from the thermal conductivity detector. It has been verified that the transistor AC 128 used in the detector circuit causes no amplification of the signal. Thus not only no amplification has been used in the case of the new detector but also the signals often represent only a fraction of the total output which is too high for the recorder. Another advantage of the new detector over the thermal conductivity one is that its sensitivity does not suffer from a rise of temperature; on the contrary, there is a marked increase in the sensitivity at higher temperatures².

The absence of metallic electrodes in the new detector distinguishes it from the other discharge detectors with metallic electrodes used by earlier workers⁴⁻⁷ which are characterised by a steadily decreasing sensitivity and poor reproducibility due to rapid contamination of the electrode surfaces by decomposition products. The electrodeless discharge is free from these limitations and it can be worked under optimum conditions when the signals are reproducible and linearly related to the quantity of the samples of a variety of gases and vapours of varied chemical nature. This high sensitivity and versatility of the electrodeless discharge detector combined with the extreme simplicity of its construction commend its adaption as a cheap and efficient detector in gas chromatography.

Acknowledgement

We thank Mr. S. S. SARDESAI for his help in constructing the detector circuit used in this work.

*Department of Chemistry,
University of Poona,
Poona-7 (India)*

H. J. ARNIKAR
T. S. RAO
K. H. KARMARKAR

- 1 H. J. ARNIKAR, T. S. RAO AND K. H. KARMARKAR, *J. Chromatog.*, 26 (1967) 30.
- 2 H. J. ARNIKAR, T. S. RAO AND K. H. KARMARKAR, *Indian J. Chem.*, 5 (1967) 480.
- 3 H. J. ARNIKAR, T. S. RAO AND K. H. KARMARKAR, *Intern. J. Electronics*, 22 (1967) 381.
- 4 J. HARLEY AND V. PRETORIUS, *Nature*, 178 (1956) 1244.
- 5 R. C. PITKETHLY, *Anal. Chem.*, 30 (1958) 1309.
- 6 S. A. RYCE AND W. A. BRYCE, *Nature*, 179 (1957) 141.
- 7 E. R. FISHER AND M. MCCARTY, JR., *Anal. Chem.*, 37 (1965) 1208.

Received August 16th, 1968