

## Gas chromatographic determination of traces of light hydrocarbons and sulphur compounds in gases at low pressure by the simultaneous use of flame ionization and flame photometric detectors

GIANRICO CASTELLO\*, GIUSEPPINA D'AMATO and MARIO NICCHIA

*Istituto di Chimica Industriale, Università di Genova, Corso Europa 30, 16132 Genova (Italy)*

(First received March 28th, 1990; revised manuscript received June 26th, 1990)

### ABSTRACT

Flame ionization and flame photometric detectors were used for the determination of light hydrocarbons and sulphur compounds in low-pressure (20–130 Pa) gases formed in radiofrequency plasma reactors. The method can be easily extended to many types of samples, such as controlled atmospheres for micro-electronic processes and polluted air. The separation of C<sub>1</sub>–C<sub>5</sub> hydrocarbons, hydrogen sulphide, carbonyl sulphide, sulphur dioxide, carbon disulphide, thiols and sulphides was tested on various columns: Carbo-pack BTH-100, Chromosil 330, Supelpak S, Chromosorb 105 and 107. The best results for the particular application, in terms of analysis speed and peak resolution, were obtained by using a short (80 cm × 2 mm I.D.) PTFE column filled with Chromosorb 105, connected by means of a 50:50 splitter to the two detectors operated in parallel. The analysis of the products formed in an ethane–sulphur dioxide plasma discharge takes about 5 min and sensitivities of 10<sup>-12</sup> g/s for hydrocarbons and 10<sup>-10</sup> g/s for sulphur compounds were achieved.

### INTRODUCTION

The application of radiofrequency plasma discharges to the surface modification of polymers and inorganic materials, by using as the feed gas mixtures of organic and inorganic compounds, has been investigated by many workers, and the determination of gaseous compounds formed in the gas phase was accomplished by using mass spectrometric and gas chromatographic techniques [1–4]. A knowledge of the purity of the gases used and the determination of the compounds formed during the reaction, which can exert catalytic or inhibitory effects on the surface reactions, is of great importance for the interpretation of the results and the study of the reaction kinetics.

Gas chromatography (GC) with specific detectors can assist in the determination of traces of organic compounds containing heteroatoms: electron-capture detector for halogens and nitro compounds, thermionic detector for nitrogen and phosphorus, flame photometric detector for sulphur and phosphorus.

In the series of experiments described here, a flame photometric detector was used to determine the amounts of hydrogen sulphide, carbonyl sulphide, thiols and

sulphides formed in a plasma discharge carried out in a feed gas composed of ethane and sulphur dioxide, which were submitted to the plasma action alone or on the surface of various polymers. The reaction of the excited species formed in the discharge with the polymer surface can yield various organic compounds containing sulphur atoms. Their identification and determination must be carried out in a low-pressure environment (between 0.2 and 1 T; 25–133 Pa) and therefore special equipment is necessary in order to deliver the sample to the analytical system.

The same methods can also be applied in the analysis of controlled atmospheres used in microelectronic production processes and, in general, when low-pressure samples have to be analysed. With some modification and simplification, the same technique can be applied to the analysis of gas mixtures at normal pressures.

## EXPERIMENTAL AND RESULTS

### *Plasma discharge unit*

Fig. 1 is a schematic diagram of the discharge unit that permitted the treatment of polymeric films with different reactive gases or the direct deposition on inert surfaces of thin layers of compounds formed in the gas phase.

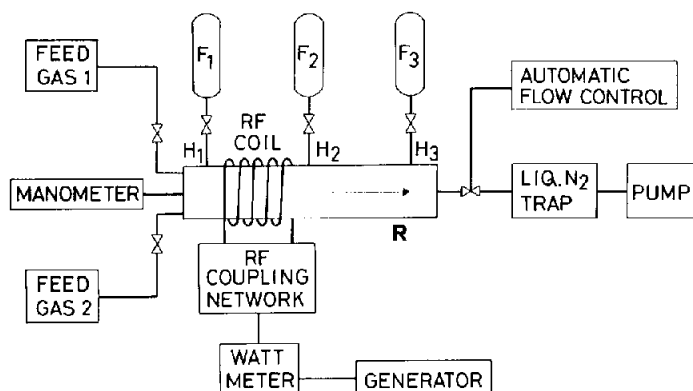


Fig. 1. Schematic diagram of the plasma generation apparatus (see text).  $H_1$ ,  $H_2$ ,  $H_3$ : pick-up points for the collection of samples in vials F or direct connection to vacuum manifold of Fig. 2.

The system was operated at a pressure of about 50 Pa with a flow-rate of 10  $20 \text{ cm}^3/\text{min}$ , obtained by continuously feeding the gas mixture at one end of the reaction tube, R, and by extracting the products and the unreacted gases at the other end with suitable vacuum pump. The plasma discharge was obtained by inductive coupling with an RF generator at a frequency of 13.5 MHz. Continuous and instantaneous samples can be taken from small tubes  $H_1$ – $H_3$  connected at various points of the reaction tube R. Samples averaged over minutes or hours of continuous discharge can be collected in evacuated vials  $F_1$ – $F_3$ .

### *Sample concentration and injection*

Fig. 2 shows the vacuum manifold used for the extraction of the gas from the

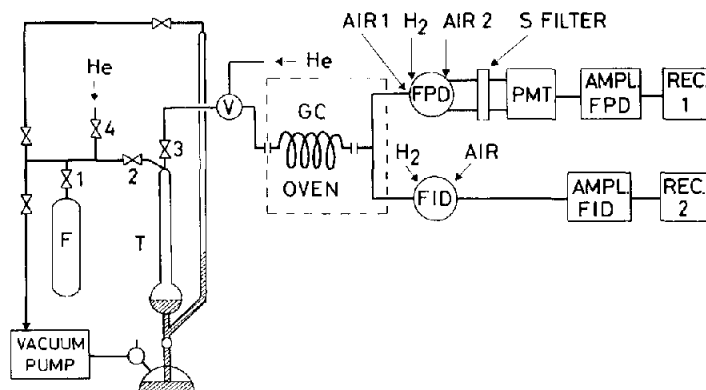


Fig. 2. Vacuum manifold used to extract low-pressure samples from vial F or directly from the RF discharge unit in Fig. 1, and to deliver them to the GC column and detectors (see text).

reaction tube or from the vials. It consists of a Toepler pump, T, where the gases can be aspirated through stopcocks 1 and 2 by lowering the mercury level.

Stopcock 2 was then closed and the mercury level raised to concentrate the gases in the upper part of T and pressurize them in order to permit the determination of their volume under known conditions of temperature and pressure, and their introduction into the gas chromatograph valve V. Pure helium supplies through stopcock 4 can be used to dilute the reaction gases in order to remain within the linearity range of the detector or pressurize them to facilitate sampling.

Stopcock 1 can be connected directly to the plasma discharge unit or to vials where the reaction products were previously collected. This manifold can therefore be used for analysis of low-pressure gas samples of any origin.

Pressurized samples (gas cylinders, gas-tight syringes, etc.) can be directly injected through valve V. Through the same valve can be injected constant volumes of standard gases prepared by using an exponential dilution flask [5,6], in order to permit an absolute calibration of the detector response.

#### *Gas chromatographic analysis*

The separation of sulphur compounds at low concentration was carried out previously by other workers by using different stationary phases: silica gel [7], graphitized carbon black treated with phosphoric acid [8], commercially available Carbowax BHT [9] or Porapak QS specially treated by washing with acetone [10], equivalent to Supelpak-S commercial phase [11]. All these phases were tested in our experiments and found to be more or less satisfactory for the separation of sulphur compounds. An additional problem arises because the selected phase must at the same time perform an efficient separation of light hydrocarbons and a fast analysis to permit a frequent check of the composition of the system under study during the evolution of the plasma discharge phenomena.

Therefore, other commercially available porous polymer bead stationary phases, (Porapak and Chromosorb Century Series) were tested by injecting standard mixtures containing both types of compounds.

As the method can be of general interest for the analysis of mixtures differing from plasma gases but containing hydrocarbon and sulphur compounds in trace amounts (refinery and paper mill effluents, waste gases, polluted industrial and town air, etc.), in the analysed samples were incorporated some gases that are probably not formed in plasma reactions but can be found in environmental samples (Table I).

The columns were made with inert tubing (PTFE) of I.D. 2 mm, filled with the following stationary phases, operated at different temperatures and flow-rates of the carrier gas: (1) Carbo-pack BHT-100 (Supelco, Bellefonte, PA, U.S.A.), 1.5 m, held isothermally at room temperature (30°C), carrier gas flow-rate 30 ml/min; (2) Chromosil 330 (Supelco), 1.5 m, operated isothermally at 40°C, carrier gas flow-rate 30 ml/min; (3) Supelpak-S (Supelco), 5 m, held isothermally at room temperature (30°C), carrier gas flow-rate 30 ml/min, temperature programme 1 min at 30°C, increased at 20°C/min to 200°C; (4) Chromosorb 105 (Johns-Manville, Denver, CO, U.S.A.), 80 cm, carrier gas flow-rate 30 ml/min, temperature programme 1 min at 60°C, increased at 20°C/min to 180°C, held for 2 min; and (5) Chromosorb 107 (Johns-Manville), same length and conditions as for column 4.

The adjusted retention times,  $t'_R$  (min), on the various columns are given in Table I. Column 1 (Carbo-pack BHT-100), a graphitized carbon black material [8,9], permitted a satisfactory separation of both sulphur compounds and hydrocarbons. Long retention times were observed for hydrocarbons  $>C_5$  and for sulphur compounds heavier than *n*-propanethiol. Under the conditions shown in Table I the following  $t'_R$  values were obtained: dimethyl sulphide, 38 min; diethyl sulphide, 56 min; *n*-butanethiol, 65 min; and *n*-hexane, 81 min; the peaks were wide, which decreased the detectivity of small amounts of substance. The overall analysis time on this column is generally too long for practical use in the rapid analysis of plasma gases.

Column 3 (Supelpak-S) is a specially washed and treated Porapak QS packing, as described by de Souza *et al.* [10,11], originally suggested for the separation of craft pulp mill exhaust gases. This packing permitted a good resolution of sulphur compounds with retention times that, under our experimental conditions, are about half of these reported by de Souza *et al.* for light compounds (hydrogen sulphide, carbonyl sulphide) and approximate the previously reported values for slow-eluting substances (dimethyl disulphide, butanethiol). Unfortunately, this column gave several interfering peaks in the hydrocarbon region.

The same effect was observed by using column 2, Chromosil 330. In this instance the rapid elution of hydrocarbons with grouped peaks may be an advantage when very small amounts of flame ionization detector-sensitive compounds have to be detected, as the minimum detectable amount increases with decrease in the peak width. Obviously, only the total amount of  $C_2$  or  $C_4$  hydrocarbons can be measured.

Columns 2 and 3 showed poor efficiency in the separation of  $C_2$  hydrocarbons, which were important components of the plasma gases used in our experiments. The separation of these compounds together with a sufficient resolution of higher hydrocarbons and sulphur compounds was carried out by using short PTFE columns (80 cm  $\times$  2 mm I.D.) filled with Chromosorb 105 porous polymer beads. This phase is an acrylic ester polymer with a surface area of 400–500 m<sup>2</sup>/g and an average pore diameter of 500 Å [12,13] and permits a rapid separation of sulphur gases with symmetrical peaks while giving an acceptable resolution between light hydrocarbons up to pentane isomers. Some inversion of the elution order of saturated and

TABLE I

ADJUSTED RETENTION TIMES  $t_R$  (min) OF LIGHT HYDROCARBONS AND SULPHUR COMPOUNDS ON DIFFERENT COLUMNS

For column preparation and analysis conditions, see text.

Compound	Column				
	(1) Carboxpack BIIT-100	(2) Chromosil 330	(3) Supelpak-S	(4) Chromosorb 105	(5) Chromosorb 107
Ethane	0.67	0.58	0.32	0.45	0.45
Ethylene	0.49	0.58	0.30	0.37	0.41
Acetylene	1.52	0.65	0.32	0.52	0.60
Propane	2.22	0.97	0.60	1.44	1.39
Propene	2.05	1.02	0.95	1.33	1.38
Isobutane	5.58	1.42	1.60	2.50	2.41
<i>n</i> -Butane	7.46	1.63	2.12	2.73	2.88
1-Butene	6.23	1.72	2.12	3.20	3.31
2-Butene ( <i>cis</i> )	9.02	1.77	2.14	3.60	3.57
2-Butene ( <i>trans</i> )	9.02	1.77	2.14	3.40	3.36
Isobutene	7.10	1.62	1.64	3.12	3.45
<i>n</i> -Pentane	24.60	2.80	3.10	4.28	4.45
Isopentane	18.50	2.56	3.07	4.10	4.17
Hydrogen sulphide	0.49	1.02	0.60	0.72	0.86
Carbonyl sulphide	1.30	0.95	0.84	1.01	1.07
Sulphur dioxide	1.22	3.93	1.62	2.03	4.18
Methanethiol	2.16	1.90	2.10	3.46	3.82
Ethanethiol	6.68	3.42	2.12	4.13	4.41
Dimethyl sulphide	7.03	3.06	5.05	4.00	4.17
Carbon disulphide	8.00	2.39	5.10	4.06	4.11
<i>n</i> -Propanethiol	22.20	7.61	4.30	12.50	13.70

unsaturated branched-chain compounds was observed with different batches of polymer and therefore the identification of these compounds should always be confirmed by injecting authentic samples. This problem has also been found with the other gas-solid or gas-gel chromatographic phases, where the mesh size, pore diameter, treatments and activation of the column may change the performance of different batches of products and their selectivity [14]. Therefore, the retention times for the fast-eluting compounds in Table I are averages from different analyses on various columns.

Moreover, the Chromosorb 105 columns showed some difficulty in separating small amounts of acetylene in the presence of a large excess of ethane. The retention time of acetylene increases with respect of that of ethane on decreasing the column temperature [15], but the slope coefficient as a function of temperature is small and therefore the separation of small amounts of acetylene from ethane is difficult. If the separation of these two gases is necessary, a column filled with Chromosorb 107 (acrylic ester polymer, surface area 400–500 m<sup>2</sup>/g, average pore diameter 80 Å) can be used.

On Chromosorb 107 acetylene has a retention index [16] ranging between 220

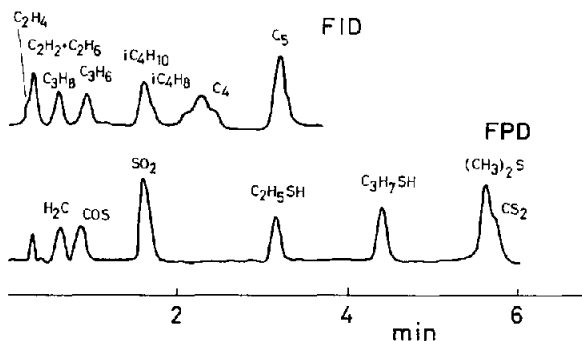


Fig. 3. Analysis of standard mixture of hydrocarbons and sulphur compounds on column 3 (Supelpak-S) with simultaneous analysis with flame ionization (FID) and flame photometric detection (FPD). For column parameters and analysis conditions, see text.

and 230 in the temperature interval used and therefore its peak is reasonably separated from that of ethane. The separation of ethylene and ethane is lightly less than that obtained on Chromosorb 105 (the retention index of ethylene is 185 on Chromosorb 105 and 190 on Chromosorb 107) but is sufficient for practical purposes [17].

Figs. 3 and 4 show the analyses of standard mixtures on Supelpak S and Chromosorb 105 (columns 3 and 4).

Fig. 5 shows a fast-eluting chromatogram obtained from an ethane-sulphur dioxide plasma. The separation of the main components of the mixture is satisfactory. Some other compounds were also detected.

Longer columns (up to 3 m) permitted a better separation of  $C_4$  compounds, but with longer retention times (up to 20 min), acceptable for the analysis of environmental samples but sometimes unsuitable for the analysis speed required to follow the evolution of the product concentrations in the RF plasma reactor.

Faster programming rates or higher final column temperatures were also to be avoided owing to the excessive noise and baseline drift on the flame photometric

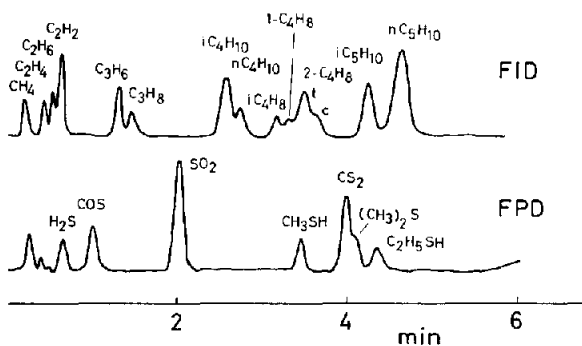


Fig. 4. Analysis of standard mixture of hydrocarbons and sulphur compounds on column 4 (Chromosorb 105) with simultaneous analysis with flame ionization (FID) and flame photometric detection (FPD). For column parameters and analysis conditions, see text.

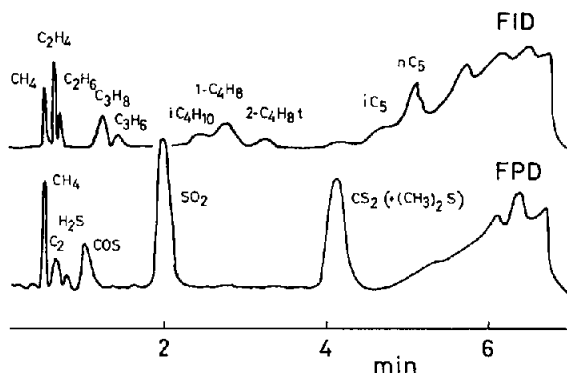


Fig. 5. Analysis of reactor plasma gas obtained from RF discharge with a 50:50 mixture of ethane and sulphur dioxide at 0.75 Torr.

detector. The use of different detectors connected in parallel (flame ionization, electron-capture, flame photometric) was previously suggested for the determination of organic pollutants in open air [18].

#### Detectors

As shown in Fig. 2, a 50:50 splitter at the end of the column, made with a Swagelok 1/8-in. T-piece connected to two short PTFE tubes (I.D. 0.8 mm), leads the eluting gases to the two detectors installed in the two bases of the heated detector oven of the Varian 3700 gas chromatograph. No differential flow control is necessary if the length of the two connecting tubes is properly adjusted in order to give the same flow-rate through the two detectors. If necessary, a variable restrictor (high-temperature needle valve; Nupro, Willoughby, OH, U.S.A.) can be installed on the flame ionization detector side of the splitter, where decomposition or reaction of sulphur compounds has a negligible effect on the detector response.

A dual flame photometric detector (Varian) was used for the determination of sulphur compounds. The first flame, used to decompose the eluting compounds and convert them into combustion products consisting of relatively simple molecules, is a "reversed" flame where a flow of air (air 1) mixed with the carrier gas coming from the column burns in a hydrogen atmosphere. The exhaust gases of the first flame, which is hydrogen rich, burn on the top of the second concentric burner, where combustion is sustained by a second air flow (air 2).

The flow-rates were air 1, 80 cm<sup>3</sup>/min; hydrogen, 80 cm<sup>3</sup>/min; and air 2, 170 cm<sup>3</sup>/min; the sum of the two air supplies is sufficient to consume approximately 50% of the hydrogen supplied to the burner and flame 2 is also a hydrogen-rich environment, where the emission of sulphur light, centred around the wavelength of 400 nm, takes place with reduced interference due to the combustion of hydrocarbons, mainly decomposed in the first flame. The light emitted was filtered through a broad-bandpass glass filter with peak transmission at 365 nm that transmitted to the photomultiplier (PMT) the low-wavelength portion of the S<sub>2</sub> emission spectra, thus reducing the interference with the CH emission lines due to thiols and residual hydrocarbons not completely decomposed in the first flame.

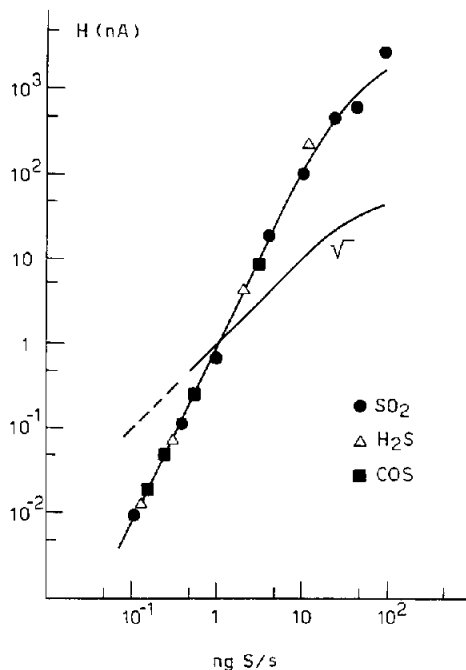


Fig. 6. Calibration graphs for the flame photometric detector obtained with an exponential dilution flask for sulphur dioxide, carbonyl sulphide and hydrogen sulphide. The line with the square-root symbol shows the response with slope = 1 obtained by using the linearizing circuit of the GC amplifier.

The detector response for hydrogen sulphide, carbonyl sulphide and sulphur dioxide was linear with slope 2.0 on a bilogarithmic plot (Fig. 6) in the range between 0.1 and 20 ng/s of sulphur.

The linear responses to other sulphur compounds (thiols, sulphides) were not tested over a wide concentration range, but the available data lie on the same straight line and therefore the calibration with a dual flame arrangement could be used for all the analysed compounds on the basis of their content of sulphur atoms. In the range 0.5–20 ng/s the quadratic attenuator built in the gas chromatograph amplifier permitted a linear response with slope 1 (shown with a square-root symbol in Fig. 6) to be obtained, thus permitting direct integration by the data system (Varian Vista 402).

For amounts smaller than 0.5 ng/s the square-root output cannot be used because it performs the square-root operation on the total detector signal, *i.e.*, the peak plus the baseline offset, which become significant with respect to small peak areas. Further, the signal processor ignores minimum signal amplitudes, and a signal and noise cutoff occurs at about a 0.5 nA detector signal at the maximum sensitivity. Amounts of sulphur below 0.5 ng/s (dashed line in Fig. 6) are therefore better measured by interpolation of the output signal on a slope 2.0 bilogarithmic plot similar to that shown in Fig. 6 but where the peak area is plotted as a function of the amount of sulphur in the sample.

Single flame operation, obtained by turning off the air supply to flame 1, was



also tested. This mode of operation decreased the linearity of the square-law dependence of the signal on the concentration and increased the quenching of the sulphur signal due to simultaneous elution of any hydrocarbon. Further, the sensitivity to sulphur atoms was dependent on the type of sulphur compound, and the advantage of a calibration that is nearly independent of the molecular structure and depends only on the number of sulphur atoms in the molecule was lost. Dual flame operation was therefore used for quantitative analysis.

Sensitivities below the ppm range were easily obtained with samples at atmospheric pressure. Concentrations of about 0.01% of sulphur compounds were found in low-pressure plasma gases.

Minimum detectable amounts of  $10^{-12}$  g/s for hydrocarbons with the flame ionization detector and  $10^{-10}$  g/s for sulphur with the flame photometric detector were found.

#### ACKNOWLEDGEMENTS

This research was supported by the Ministero Pubblica Istruzione with research funds ex art. 65, DPR 11.7.81, n. 382. The authors thank Dr. T. C. Gerbino for quantitative calibrations with an exponential dilution flask.

#### REFERENCES

- 1 G. Smolinsky and M. J. Vasile, *J. Mass Spectrom. Ion Phys.*, 21 (1976) 171.
- 2 M. J. Vasile and G. Smolinsky, *J. Mass Spectrom. Ion Phys.*, 24 (1977) 11.
- 3 G. Castello, P. Canepa and M. Nicchia, *Ann. Chim. (Rome)*, 67 (1977) 149.
- 4 G. Castello, *J. Chromatogr.*, 244 (1982) 271.
- 5 J. E. Lovelock, in R. Scott (Editor), *Gas Chromatography 1960*, Butterworths, London, 1960.
- 6 C. H. Hartmann and K. P. Dimick, *J. Gas Chromatogr.*, 6 (1966) 163.
- 7 W. L. Thornsberry, Jr., *Anal. Chem.*, 43 (1971) 452.
- 8 F. Bruner, A. Libertì, M. Possanzini and I. Allegrini, *Anal. Chem.*, 44 (1972) 2070.
- 9 F. Bruner, P. Cicciolelli and F. di Nardo, *J. Chromatogr.*, 99 (1974) 661.
- 10 T. L. C. de Souza, D. C. Lane and S. P. Bhatia, *Anal. Chem.*, 47 (1975) 543.
- 11 T. L. C. de Souza, *J. Chromatogr. Sci.*, 22 (1984) 470.
- 12 S. B. Dave, *J. Chromatogr. Sci.*, 7 (1969) 389.
- 13 S. B. Dave, *Ind. Eng. Chem., Prod. Res. Dev.*, 14 (1975) 85.
- 14 G. Castello and G. D'Amato, *J. Chromatogr.*, 349 (1985) 189.
- 15 G. Castello and G. D'Amato, *J. Chromatogr.*, 212 (1981) 261.
- 16 E. Kovats, *Helv. Chim. Acta*, 4 (1968) 1915.
- 17 G. Castello and G. D'Amato, *J. Chromatogr.*, 243 (1982) 25.
- 18 P. Cicciolelli, G. Bertoni, E. Brancaloni, R. Fratarcangeli and F. Bruner, *J. Chromatogr.*, 126 (1976) 757.