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USE OF CHLORPYRIFOS AS AN EVALUATION STANDARD FOR GAS CHROMATOGRAPHIC DETECTORS

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SUMMARY

The performance of a range of element-selective detectors was studied using chlorpyrifos (O,O-diethyl-O-3,5,6-trichloro-2-pyridyl phosphorothioate) as a standard. It involved determination of the minimum detectable amount and linearity of the response of the flame photometric, alkali flame ionization, Hall electrolytic conductivity and electron capture detectors.

The minimum detectable amount varied with both the model and type of detector, with the electron capture detector (frequency-modulated mode) being the most sensitive and the flame photometric detector (S-mode) the least. A study of various models of electron capture detector demonstrated the superior performance of the frequency-modulated type to the d.c. or d.c. pulse mode in both sensitivity and linearity. The responses of various types of alkali flame ionization detector were similar and *ca.* 10 times more sensitive than the flame photometric detector (P-mode). The N/P response of the alkali flame ionization detector was dependent on the hydrogen flow-rate. The multi-element response of the detector is suppressed by using a flame energized source. The response of the flame photometric detector to chlorpyrifos analogues showed a variation in the minimum detectable amount of 2.1-4.5 for the P=O/P=S ratio, which indicated it to be a detector effect.

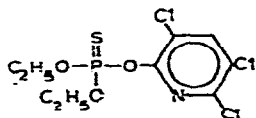
The results obtained warrant the consideration of chlorpyrifos as a common evaluation standard for the sensitivity and linearity data of gas chromatographic detectors used in pesticide residue analysis.

INTRODUCTION

Information regarding the performance of gas chromatographic (GC) detectors is of interest to the analyst concerned with the choice of equipment, the suitability of an analytical procedure or the amount of sample clean-up necessary. Detector performance is usually described in terms of sensitivity, selectivity, limit of detection

and linearity of its response. Although the literature abounds with such data¹⁻⁶, it is often difficult to correlate for comparative purposes because of the multiplicity of reference standards used. This problem applies especially to the evaluation of element selective detectors, such as the flame photometric (FPD), alkali flame ionization (AFID) and Coulson (CECD) or Hall electrolytic conductivity (HECD).

The desirability of reporting detector performance in some standard manner was emphasized as early as 1957⁷. Although various proposals have been advanced in the intervening years⁸⁻¹⁰, no standard protocol has yet been adopted. As more interlaboratory comparative studies with detectors are carried out, so the need for a common performance standard increases. The use of chlorpyrifos (O,O-diethyl-O-3,5,6-trichloro-2-pyridyl phosphorothioate) has been previously suggested as a standard reference compound for the comparison of sensitivity and linearity data¹¹. It has the advantage that it contains the heteroatoms Cl, N, P and S which enable it to be used with all the various element-selective detectors used in residue analysis today.



In addition, it is a stable compound, has good GC characteristics and can be detected by the electron capture detector (ECD). This paper reports further on its application for evaluating the sensitivity and linearity of various types and models of GC detectors. Comments are made on the response of chlorpyrifos and its analogues with a multi-element selective AFID detector.

EXPERIMENTAL

The work was carried out using various Pye model 104 gas chromatographs fitted with Pye 3-electrode AFID (RbCl), FID, d.c. pulse mode and frequency-modulated ECD. A Bendix SPED (FPD), and a Perkin-Elmer NPD (AFID) were also adapted for use with this gas chromatograph. In addition a Hewlett-Packard Model 5713 equipped with frequency-modulated ECD and NPD (AFID), and a Microtek MT220 fitted with a HECD were used in the study.

All the glass columns used had similar dimensions, 2.3 m \times 4 mm I.D., packed with 100-120 mesh Gas-Chrom Q coated with 3% OV-17. The columns were extensively conditioned by heat¹² and repeated injection of the compounds under study, before the response factors were determined. The latter was especially important for the oxons. All responses reported are the average of five replicate injections.

Analytical standards of chlorpyrifos and its oxon were obtained from Dow Chemical, Midland, Mich., U.S.A. The analogues, O,O-diethyl-O-3,5,6-trichlorophenyl phosphorothioate, O,O-diethyl-O-2-pyridyl phosphorothioate; O,O-diethyl-O-phenyl phosphorothioate and the oxons were prepared by standard methods involving reaction of the sodium salt of the corresponding phenol with O,O-diethyl phosphoro- and phosphorothio-chloridate. The products were characterized by NMR and GC following purification by column chromatography and vacuum distillation. All the compounds had a purity of 98%.

RESULTS AND DISCUSSION

The sensitivity of a GC detector is directly related to the efficiency with which a sample is converted into the species detected. For ionization detectors it is measured as the response in coulombs/gram. Alternatively, detector performance may be expressed as the minimum detectable amount (MDA). The latter has been arbitrarily accepted as the amount of material injected which gives a response equivalent to twice the noise level and is usually expressed in units of g/sec or g atom/sec¹.

In practice, the MDA is preferred to sensitivity since it is based on peak height and takes into account the noise level of the detector. The difference between the two can be illustrated by comparison of the response of the Pye AFID and the Perkin-Elmer NPD (P-mode), where the sensitivities were found to be 105 and 10 C/gP and the noise levels were 1 and 8×10^{-2} pA, respectively. This results in both detectors having a similar MDA for chlorpyrifos although the sensitivities differ by a factor of 10.

The MDA values for chlorpyrifos determined with various types of selective element detectors are given in Table I. The values differ according to the type of detector with the ECD being the most sensitive and the FPD (S-mode) the least. However, the data indicates that chlorpyrifos is sufficiently sensitive to all types of detectors to warrant its use as a common standard. Comparing the three FPDs, these MDAs are very similar in the P-mode (526 nm) but vary in the S-mode (394 nm). The poor sensitivity of the Bendix SPED (S-mode) in this case was attributed to the fibre optics, which showed reduced light transmission with extended use at high temperature (230°). The AFIDs examined included the Pye AFID, which has a flame-heated RbCl source, and the Hewlett-Packard and Perkin-Elmer NPDs, which operate with an electrically heated source. The responses of the various types of AFIDs to chlorpyrifos are similar and approximately 10 times more sensitive than for the FPD (P-mode). It is of interest to note that the HECD in the halogen mode is as sensitive to chlorpyrifos (3 Cl) as the FPD in the P-mode.

Chlorpyrifos was employed as the reference standard for an interlaboratory study to determine the sensitivity of ECDs used in routine residue analysis¹³. Each

TABLE I

THE MINIMUM DETECTABLE AMOUNT OF CHLORPYRIFOS DETERMINED ON VARIOUS TYPES OF GC DETECTOR *

Detector	MDA (pg/sec)	Detector	MDA (pg/sec)
AFID		FPD	
Pye	0.12	Trator (P)	2.4
Perkin-Elmer (NP)	0.13	(S)	4.0
(P)	0.15	Bendix (P)	2.1
Hewlett-Packard (NP)	0.12	(S)	107
		Pye (P)	1.0
		(S)	32
HECD		ECD	
(halogen)	2.32	Pye	0.01
		(frequency-modulated)	

* Mode of operation given in parenthesis: NP, nitrogen/phosphorus; P, phosphorus; halogen, chlorine; S, sulfur.

laboratory was asked to determine the MDA of chlorpyrifos (standard supplied) under their own conditions of operation. The results from the various types of ECD design (Table II) show surprisingly good agreement. In general, the frequency-modulated ECDs (constant current) were more sensitive than the d.c. or d.c. pulsed mode ECDs (constant frequency), especially when nitrogen was employed as the carrier gas. The only direct comparison of the two carrier gases, argon-methane and nitrogen, was made with the Analog Technology Corp. (ATC) detector, which gave MDA of 0.012 and 0.007 pg/sec, respectively. A larger pulse width is required for nitrogen (0.6 μ sec) than for argon-methane owing to the slow diffusion rate of the ions. The responses of the two d.c. detectors, one with a ^{63}Ni and the other a ^3H source were similar, but both were less than that obtained with the frequency-modulated detectors.

TABLE II

INTERLABORATORY STUDY OF THE MDA OF CHLORPYRIFOS BY d.c.-PULSED AND FREQUENCY-MODULATED ECDs*

Frequency-modulated detectors			d.c. or d.c.-pulsed detectors		
Detector	Carrier gas	MDA (pg/sec)	Detector	Carrier gas	MDA (pg/sec)
HP 5739	argon-methane	0.015	MT 220	nitrogen	0.07
5713	argon-methane	0.05	MT 220	nitrogen	0.03
5710	argon-methane	0.07	MT 220	nitrogen	0.11
5710	argon-methane	0.02	MT 220	nitrogen	0.08
5710	argon-methane	0.04	MT 220	nitrogen	0.14
ATC 2**	argon-methane	0.012	MT 220	nitrogen	0.04
		Av. 0.034			Av. 0.078
ATC 2**	nitrogen	0.007	Varian***	nitrogen	0.01
MT 290	nitrogen	0.009	Varian	nitrogen	0.09
Fisher	nitrogen	0.003	Varian	nitrogen	0.20
MT 550	nitrogen	0.04	Varian	nitrogen	0.01
GCD	nitrogen	0.04	Varian	nitrogen	0.03
		Av. 0.019			Av. 0.068

* Except where indicated ^{63}Ni ECDs were employed.

** Scandium ^3H .

*** ^3H .

The main advantage of the frequency-modulated ECD lies in the extended linear range, which facilitates the use of this detector with automated analysis. The difference in linearity when operating d.c.-pulse and frequency-modulated modes is illustrated in Fig. 1 for the Pye 104 ECD. With nitrogen as the carrier gas, the detector is linear for a 10^4 range of concentration in the frequency-modulated mode, as opposed to 10^2 - 10^3 in the d.c.-pulse mode. A direct comparison of the sensitivities in the two modes is difficult, being dependent on the detector current setting in the frequency-modulated mode and pulse spacing in the d.c.-pulse mode. The increased sensitivity in the d.c.-pulse mode observed with increasing pulse space (Fig. 1) is compound dependent and is the result of greater reaction time allowed before collecting the ions¹⁴.

The AFIDs respond to both nitrogen- and phosphorus-containing insecticides and herbicides. They are, however, more sensitive to phosphorus than nitrogen. The

response of the Perkin-Elmer AFID to chlorpyrifos and atrazine is shown in Fig. 2 when operated in both the P and NP modes. In the P-mode, the alkali source is energized by a high energy flame, as opposed to the source being electrically heated in the NP-mode. The response to phosphorus is effectively the same in the two modes, whereas the nitrogen response is suppressed *ca.* 50-fold in the P-mode, relative to the NP-mode.

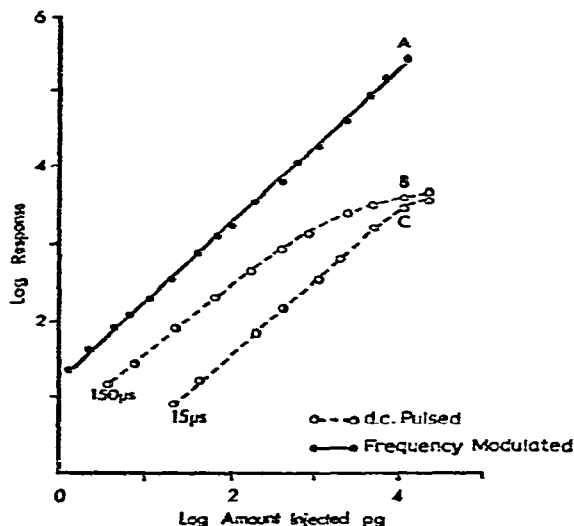


Fig. 1. Linearity of a Pye 104 ECD operating (a) in the frequency-modulated mode (b) d.c.-pulse mode, 150- μ sec pulse space and (c) d.c.-pulse mode, 15- μ sec pulse space, for chlorpyrifos.

The AFID response to nitrogen compounds has been reported to be proportional to the alkali ion concentration in the plasma and inversely proportional to the hydrogen flow-rate¹⁵. In the case of chlorpyrifos, the response increased with both hydrogen flow-rate and standing current. This effect is shown in Fig. 3 for atrazine (N) and chlorpyrifos (N,P) and diethylphenyl phosphorothioate (P) with the Perkin-Elmer AFID in the NP-mode. The result shows that the optimum flow-rate for the nitrogen compound is 2–3 ml/min, in agreement with the work of Kolb *et al.*¹⁶ who suggested an optimum of 1–3 ml/min hydrogen flow-rate. Chlorpyrifos, although it contains both nitrogen and phosphorus, responds as a phosphorus compound, which has an optimum hydrogen flow-rate of 4–5 ml/min. These results indicate that the P/N selectivity is not constant, being dependent on the hydrogen flow-rate. Calculations based on the sensitivity of chlorpyrifos and atrazine indicate that it is three times greater at 5 ml/min than 1 ml/min hydrogen flow-rate. This detector in the NP-mode has a linear range of 10^5 for both chlorpyrifos and atrazine, whereas in the P-mode for chlorpyrifos it is reduced to 10^4 (Fig. 4). The linear range was similar for the Pye and Hewlett-Packard AFIDs, using chlorpyrifos as the standard.

Although the HECD is principally used as a selective nitrogen detector in residue analysis, it can also function as a halogen selective detector. This is achieved by operating in the reducing mode using hydrogen reaction or carrier gas and no catalyst. The linear range for chlorpyrifos (3 Cl) is compared with that of lindane

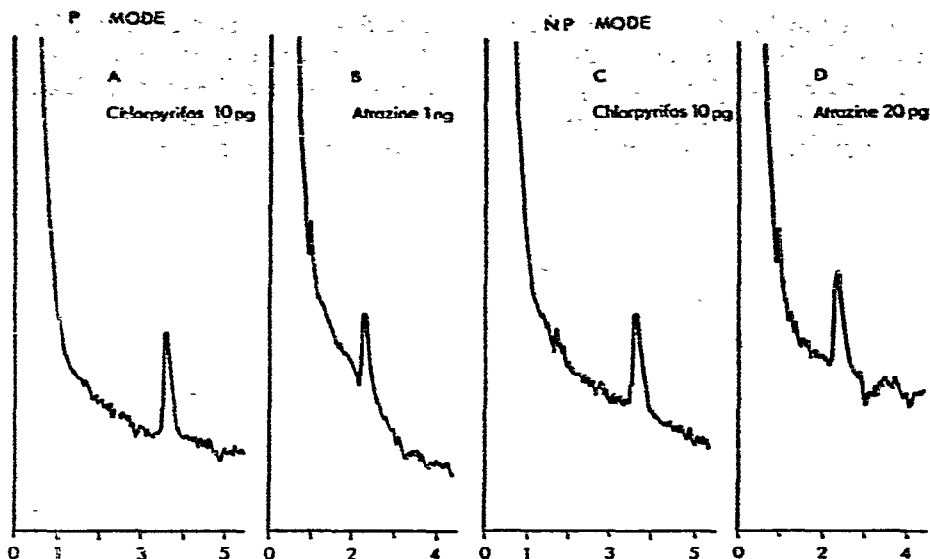


Fig. 2. Chromatograms of chlorpyrifos and atrazine obtained with a Perkin-Elmer NPD (AFID) operating in the P-mode (a) chlorpyrifos 10 pg, (b) atrazine 1 ng and in the NP mode, (c) chlorpyrifos 10 pg and (d) atrazine 20 pg. Conditions: P-mode, carrier 30 ml/min nitrogen; detector 34 ml/min hydrogen, 25 ml/min air; NP-mode, carrier 30 ml/min helium; detector, 3 ml/min hydrogen, 100 ml/min air, standing current 3 pA.

(6 Cl) in Fig. 5. As expected, the response to lindane is greater than for chlorpyrifos but the linear range of 10^5 is the same and similar to that reported by Hall¹⁷. Recently, a screening procedure for carbamates and urea herbicides using the heptafluoropropyl derivatives has been reported using this mode¹⁸. In the reductive mode with hydrogen reaction gas and nickel catalyst, the detector can be made selective to nitrogen

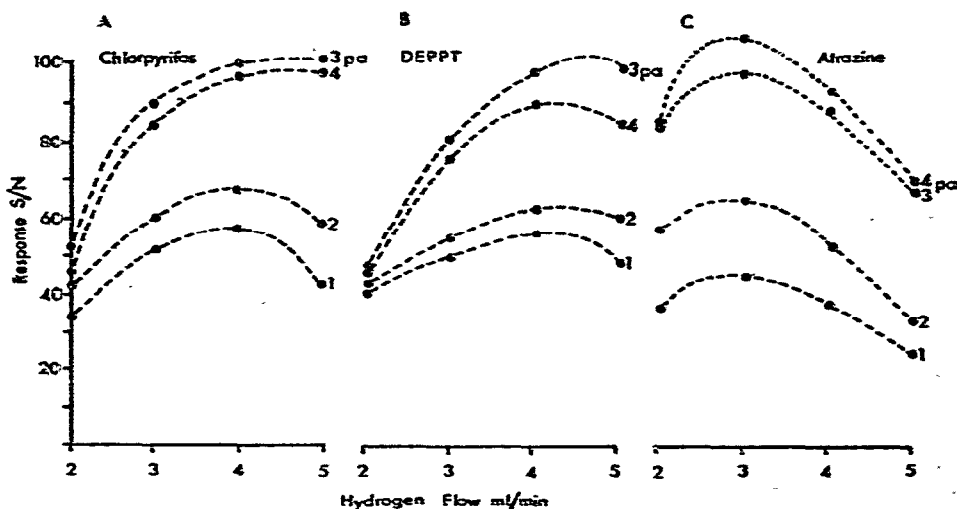


Fig. 3. Variation of the response (signal/noise) with hydrogen flow-rate and standing current with a Perkin-Elmer NPD (AFID) in the NP mode for (a) chlorpyrifos, (b) diethyl phenyl phosphorothioate (DEPPT) and (c) atrazine.

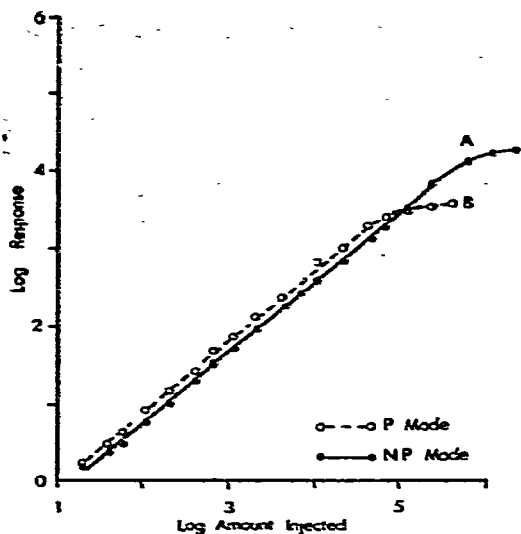


Fig. 4. Linearity of a Perkin-Elmer NPD (AFID) operating (a) in the NP-mode and (b) in the P-mode for chlorpyrifos. Conditions as in Fig. 2.

reaction gas and nickel catalyst, the detector can be made selective to nitrogen by removal of the HCl and H₂S formed using a strontium hydroxide scrubber. A linear range of only 10²-10³ was obtained in the nitrogen mode for chlorpyrifos. Difficulties were experienced in obtaining reproducible results in the nitrogen mode, particularly at low levels of chlorpyrifos (<20 ng). The results were obtained on one

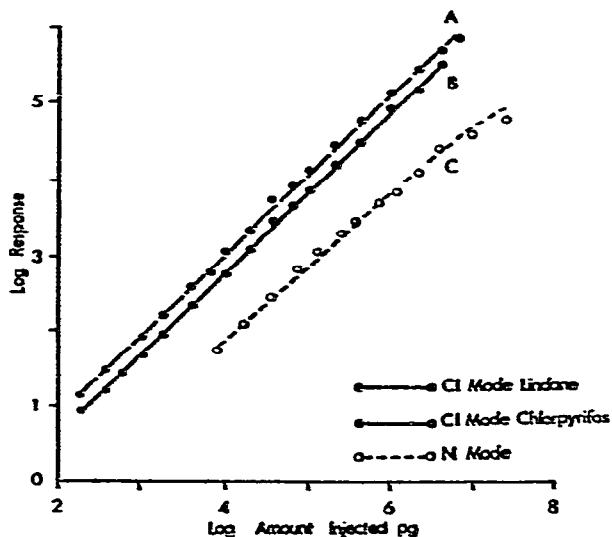


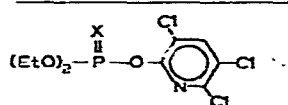
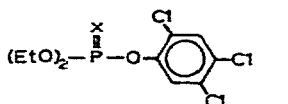
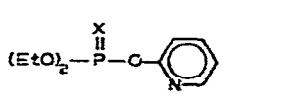
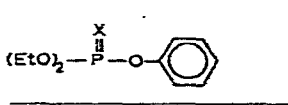
Fig. 5. Linearity of the Hall ECD operating in the halogen mode for (a) lindane and (b) chlorpyrifos, and (c) in the N-mode for chlorpyrifos. Conditions: N-mode, carrier 70 ml/min helium, reactor gas 30 ml/min hydrogen; furnace temp. 900°; nickel catalyst with Sr(OH)₂ scrubber; solvent, 50% 2-propanol-water, 0.7 ml/min. Halogen mode, carrier 40 ml/min helium, reactor gas 20 ml/min hydrogen; furnace temp. 850°; solvent 50% 2-propanol-water, 0.2 ml/min.

of the first commercial models produced in 1974¹⁹ and since then two commercial modifications of this detector have been produced.

Response of a GC detector depends on the efficiency of formation of the activated species measured, such as HPO in the case of the FPD (P-mode). The atoms attached to phosphorus will affect this process depending on the decomposition reaction and the bond energies involved. With the AFID, the sensitivity to phosphorothioates (P=S) is greater than to the oxon analogues (P=O), also substitution of the oxygen atoms attached to phosphorus by nitrogen results in a progressive reduction in sensitivity²⁰. Using an OV-17 column, the effect on the response of the Bendix SPED (P-mode) of various chlorpyrifos analogues, involving changes of substitution at phosphorus and in the phenyl moiety, was examined. The MDA for the analogs are shown in Table III. Substitution in the phenyl moiety of the phosphorothioates has only a small effect on the sensitivity, but an appreciable effect in the case of the phosphates. The P=O/P=S ratio varies from 4.5 for chlorpyrifos to 2.1 for diethylphenyl phosphorothioate. The response was also determined on the more polar DEGS phase, which gave similar values. These results indicate that the variation in response is a detector rather than column effect. Replacement of the sulfur by an oxygen atom in the P=X bond appreciably reduced the formation of the measurable species. Substitution of the phenyl moiety produces only a minor effect on the phosphorothioates but a major one on the phosphates.

TABLE III

RESPONSE (LDA) OF BENDIX SPED (P-MODE) TO CHLORPYRIFOS ANALOGUES

Structure	Minimum detectable amount (pg P/sec)		P = O/P = S ratio
	Thion (X = S)	Oxon (X = O)	
	0.177	9.796	4.5
	0.164	0.517	3.15
	0.248	0.806	3.25
	0.15	0.32	2.1

In summary, the response of both element- and group-selective detectors to chlorpyrifos varies according to the type of detector. Similar linear ranges are obtained when standards containing one specific heteroatom are compared on different element-selective detectors. Because of the latter fact and its sensitivity to these

detectors, chlorpyrifos is recommended as a common standard for the evaluation of GC detectors.

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REFERENCES

- 1 C. H. Hartmann, *Anal. Chem.*, 43 (1971) 113A.
- 2 J. Ševčík, *Detectors in Gas Chromatography*, Elsevier, Amsterdam, 1976.
- 3 A. R. L. Moss, *Pye Scan.*, 4 (1964) 5.
- 4 D. F. S. Natush and T. Thorpe, *Anal. Chem.*, 45 (1973) 1185A.
- 5 D. J. David, *Gas Chromatographic Detectors*, Wiley-Interscience, New York, 1974.
- 6 L. S. Ettre, *J. Chromatogr. Sci.*, 16 (1978) 396.
- 7 D. H. Desty, *Nature (London)*, 179 (1957) 241; 180 (1957) 22.
- 8 H. W. Johnston, Jr. and F. H. Stross, *Anal. Chem.*, 31 (1959) 1206.
- 9 G. L. Sutherland, *Residue Rev.*, 10 (1965) 85.
- 10 R. K. Skogerbee and C. L. Grant, *Spectrosc. Lett.*, 3 (1970) 215.
- 11 W. P. Cochrane and R. Greenhalgh, *Chromatographia*, 9 (1976) 225.
- 12 W. P. Cochrane, B. P. Wilson and R. Greenhalgh, *J. Chromatogr.*, 75 (1973) 207.
- 13 W. P. Cochrane, R. B. Maybury and R. Greenhalgh, *J. Environ. Sci. Health*, B14 (1979) 197.
- 14 F. W. Karasek, O. S. Tatone and D. M. Kane, *Anal. Chem.*, 45 (1973) 1210.
- 15 B. Kolb and J. Bischoff, *J. Chromatogr. Sci.*, 12 (1976) 621.
- 16 B. Kolb, M. Aver and P. Pospisil, *J. Chromatogr. Sci.*, 15 (1977) 53.
- 17 R. C. Hall, *J. Chromatogr. Sci.*, 12 (1976) 152.
- 18 J. E. Lawrence and J. J. Ryan, *J. Chromatogr.*, 130 (1977) 97.
- 19 B. P. Wilson and W. P. Cochrane, *J. Chromatogr.*, 106 (1975) 174.
- 20 R. Greenhalgh and W. P. Cochrane, *J. Chromatogr.*, 70 (1972) 37.