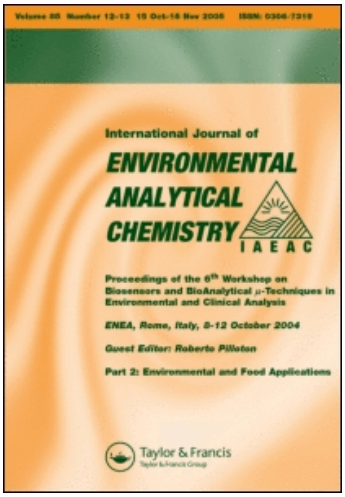

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A Library Report on the Analysis of Pesticides Subject to Investigation for the European Communities Commission

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A LIBRARY REPORT ON THE ANALYSIS OF PESTICIDES SUBJECT TO INVESTIGATION FOR THE EUROPEAN COMMUNITIES COMMISSION

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A recent Report from the Commission of the European Communities indicated a list of eleven pesticides (benazolin, bromofenoxim, ethofumesate, fenamiphos, maneb, metham-sodium, oxydemetonmethyl, phenmedipham, trichlorfon, trichloroacetic acid, ziram) to be studied on an analytical point of view because of their widespread use in Europe, but which lack of suitable analytical procedures for water samples at the required limit of detection (0.1 μg/l).

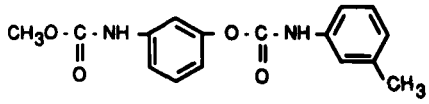
The present study presents the results of a library search, and indicates the principal procedures presented in the literature for these pesticides. Useful techniques appeared for some compounds, but for others more studies are still needed.

KEYWORDS: Pesticides, library search, GC, HPLC, mass spectrometry, water.

INTRODUCTION

Recently the European Communities Commission published a Report on "*Pesticides in ground and drinking waters*"[1] that indicated the need to study better the analytical procedures for 11 pesticides that are widely used in Europe. These are: benazolin, bromofenoxim, ethofumesate, fenamiphos, maneb, metham-sodium, oxydemetonmethyl, phenmedipham, trichlorfon, trichloroacetic acid (TCA), ziram (Figure 1). Our Institute was asked to study the matter in collaboration with six other European laboratories.

Starting our task on the development of suitable analytical procedures, we considered the studies present in the literature. A computerized search was conducted through Chemical Abstracts on-line from 1967 to 1992 (upgrading is in progress). To obtain a wider information base, the search was not limited to the analysis of water samples.



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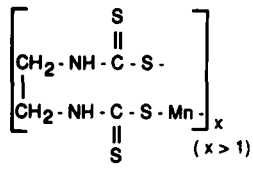

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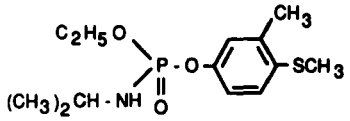

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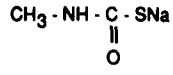
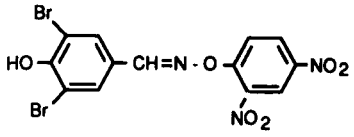


Metham-Sodium



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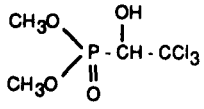
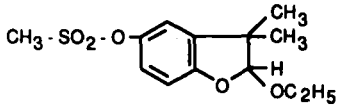


Trichlorfon



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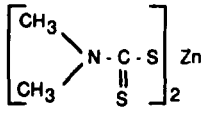

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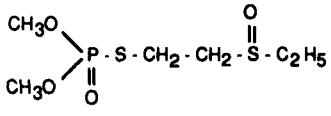
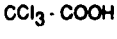
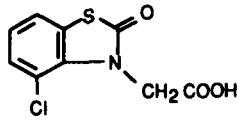


Oxydemeton-methyl



TCA



Benazolin

Figure 1 Chemical structures of the 11 pesticides considered in the library search.

COMPUTER SEARCH

The search was conducted using the Chemical Abstracts (the American Chemical Society bibliographic database) on-line version through the European host computer Data-Star. We extended the search back to 1967 using the Chemical Abstract Service (CAS) registry

number for each compound plus the free text words "gas chromatography" (GC), "liquid chromatography" (HPLC) and "mass spectrometry" (MS). We applied all possible synonyms plus truncations.

RESULTS

All the papers dealing with GC and HPLC methods and these 11 compounds were considered (277 papers). No reports were found for **bromofenoxim** and a few of the references for the other pesticides were not pertinent (TCA, for example, is sometimes used in the mobile phases of HPLC methods). Table 1 shows an overview of the 11 pesticides and their references, divided according to the chromatographic methods GC and HPLC. Studies dealing with water analyses have also been listed. GC and HPLC techniques are summarized in Tables 2 and 3. MS detection, when coupled with these chromatographic techniques, was considered with particular attention.

We then considered the results for each compound with particular attention to the analytical method(s) applied. Some references had to be overlooked because of the difficulty of obtaining the original paper or a translation of the text.

Ethofumesate

There were five reports, three dealing with HPLC analysis and two with GC. Two considered water analysis, one by GC-MS[2] and the other by HPLC[3]. Legrand *et al.*[2] measured this and 37 other pesticides in French surface and ground waters at or below 100 ng/l and reported their recovery results with liquid-liquid extraction (LLE) (always more than 80%).

GC analysis: in the above study[2] a moving needle injector was used with a DB5 30m capillary column and a MS detector in the selected ion monitoring (SIM) mode employing

Table 1 Results of a library search on chromatographic methods for the pesticides considered. The number of reports are indicated. Main references for water analysis are reported.

Compound	*Total*	*GC*	*HPLC*	*TLC*	*water*[ref]
Ethofumesate	5	2	3	-	2[2,3]
Trichlorfon	86	71	14	4	5[7–9]
Fenamiphos	21	14	7	-	7[39–44]
Oxydemetonmethyl	22	17	3	2	-
Bromofenoxim	-	-	-	-	-
Benazolin	1	1	-	-	-
Maneb	13	8	6	-	-
Metham sodium	9	1	8	-	2[57,58]
Metham acid	1	-	1	-	-
Ziram	13	5	8	-	1[63]
Phenmedipham	30	8	21	1	7[68–71]
Trichloroacetic ac.	77	44	6	-	11[77–83]

Table 2 Results of a library search considering GC analysis.

Compound	Injector (ref.)	Column (ref.)	Detector (ref.)	GC-MS (ref.)	Deriv. (ref.)
Ethofumesate	moving needle (2);	packed: OV101 (4); capillary: DB5 (2);	FID (4);	EI ionization: SIM (2);	no report
Trichlorfon	Hot, cold splitless and on column (10);	capillary: SE30, SE54, OV101 (10, 11); megabore: SPB5 (8, 12); chiral capillary: (14); packed: (13);	FID (4); TID (15, 16); NPD (12); ECD (18); FPD (13, 17); double detection: FPD and ECD (19), electrolytic conductivity det. and FPD (20);	EI ionization: positive in SIM (7, 9, 21–24); CI: pulsed positive negative in SIM (11);	acethylation (25, 26); silylation (27);
Fenamiphos	split (45);	packed: (13); NPD (42); capillary: SE30, SE54 OV101 (11, 45);	ECD and TID (45); CI: ion trap det. (40), FPD and electrolytic conductivity det. (16);	EI ionization: (46); pulsed positive negative det. (11);	no report
Oxydemetonmethyl	split/splitless (11, 4);	packed: OV101 (4); capillary: SE54, SE30, OV101 (11);	FID (4); FPD and electrolytic conductivity det. (20);	EI ionization: (46), SIM (23); CI: pulsed positive negative det. (11);	trifluoro acethyl (49);
Bromofenoxim	no report	no report	no report	no report	no report
Benazolin	split/splitless (51);	capillary: DB1 (51);	NPD (51);	EI ionization: (51);	(2-cyanoethyl) dimetyl(diethylamino) silane (51);
Maneb	Head-space (52, 53);	capillary: Cp Sil8 (52); packed: (53);	ECD (52); FPD (53);	no report	no report
Metham sodium	charcoal trapping (56);	capillary: Cp Sil5 (56)	FID and NPD (56);	no report	no report
Metham acid	no report	no report	no report	no report	no report
Ziram	head space (64); splitter (65);	capillary: SE30, OV101 (65);	FID (65);	no report	no report
Phenmedipham	split/splitless (72);	capillary: HP1 (72);	NPD (72); FID (4);	EI ionization: (72);	acetic anhydride (72);
Trichloroacetic acid	head space (84, 85); splitless (78, 86, 87);	packed: (78, 86, 88); capillary: SE30, OV351 (87, 89);	FID (86, 89); ECD (78, 87, 88); plasma emission det. (82);	CI: positive SIM (90);	diazomethane (88, 90); difluoroanilide (78); pentafluorobenzyl (87); monochloroalkyl esters (89);

Table 3 Results of a library search considering HPLC analysis.

Compound	column (ref.)	detector (ref.)	HPLC-MS (ref.)	pre col.derivatiz. (ref.)
ethofumesate	reversed phase (3, 5, 6)	UV (3); fluorescence (5);	no report	no report
Trichlorfon	**reversed phase (30, 31);** normal phase (32);	UV: (33); UV-post col. **reaction (34);** TID (37);	post col. extraction (32); **TSP-MS (35, 36);** MS-MS (38);	**no report**
Fenamiphos	reversed phase (41);	UV (41); UV-post col. reaction fluorescence (47);	TSP-MS (44);	no report
oxydemetonmethyl	reversed phase (30, 31);	electrolytic conductivity det. (50);	no report	no report
Bromofenoxim	no report	no report	no report	no report
Benazolin	no report	no report	no report	no report
Maneb	reversed phase (54);	UV (54); post col. reaction det. (55);	no report	methylation (54);
Metham sodium	reversed phase: RP18 (54), micellar mobile phase (57, 59), ion pair reagents (60);	UV (54); UV diode array det. (58); fluorometric det. (61);	no report	methylation (54);
Metham acid	normal phase (62);	UV (62);	no report	metal chelate der. (62);
Ziram microcolumn (67);	reversed phase: RP18 (54), plasma emission det. normal phase: microcolumn (67);	UV (54); particle beam-MS (63); (67);	cobalt complex (66);	methylation (54);
Phenmedipham	reversed phase: C18 (61), gradien elution (73), direct liquid introduction (74);	UV (68); post col. reaction- fluorometric det. (61); electrochemical det. (75);	field des.-MS (69); TSP-MS (76)	no report
Trichloroacetic acid	reversed phase: iron complex in mobile phase (91), ion pair and ion exchange (92), amino col. (93);	UV fluorescence-post col. reaction (94);	no report	no report

electron impact (EI) ionisation. Other authors[4] employed packed columns with a flame ionization detector (FID).

HPLC analysis: reversed phase columns were used, with a UV or fluorescence detector[3,5,6].

Trichlorfon

We found 86 reports, 71 using GC and 14 HPLC, and five of them considered water analysis[7–9]. No extraction (lower than 5%) was obtained when LLE was used with methylene chloride[9], but recovery was more than 80% by SPE using XAD-4 resin[8].

GC analysis: a major problem in the GC analysis of trichlorfon is its thermal instability, particularly in the injection port. Different injection methods have been tried: hot and cold splitless (PTV) and on-column injections, using a SE54 capillary column[10]. Other capillary columns were used: SE30 and OV101[11] or megabore SPB5[8,12]; nine different kinds of packed column have been tested[13]. A chiral capillary column containing modified cyclodextrin as stationary phase was employed to separate the two enantiomers[14]. This study used the FID as did Saxton[4]. Other detectors were used in trichlorfon analysis: thermoionic detectors (TID)[15,16], nitrogen-phosphorus detector (NPD)[12], flame photometric detector (FPD)[13,17], electron-capture detector (ECD)[18] and in some cases double detection, FPD with ECD[19] or electrolytic conductivity detector with FPD[20].

Twelve reports were found on GC-MS analysis, mainly with EI ionisation and in SIM[7,9,21–24], but one study used chemical ionization (CI) with SIM by pulsed positive/negative detection, for confirmation purposes[11]. GC analysis was also carried out after acetylation[25,26] and silylation[27]. Vilceanu *et al.*[26] studied the kinetics of acetylation and a 4:1 ratio between acetic anhydride and pyridine proved to be the best to attain complete derivatization of trichlorfon after 50 min at room temperature, avoiding the formation of by-products.

HPLC analysis: Both reversed and normal phases were tested[28–32]; UV detection was used directly[33] or after post-column reaction[34], while Gluckman *et al.*[37] used reverse phase narrow-bore columns with on line TID. Seven studies used mass spectrometry coupled with HPLC, and some with a TSP interface,[35,36] also after a post-column extraction system[32]. Betowski *et al.* analyzed trichlorfon and other organophosphorus pesticides by HPLC-MS and HPLC-MS/MS[38].

Fenamiphos

We found 21 reports concerning this pesticide, 14 in GC and seven in HPLC; seven were on water analysis[39–44]. Di Corcia *et al.* obtained 95% recovery by SPE with Carbopack B from groundwater at 0.1 ppb using an HPLC-UV analytical system, and their LOD was 0.01 ppb[41].

GC analysis: Split injection was commonly used[45], with different capillary columns, SE30, SE54 and OV101[11,45]. Prinsloo *et al.* analyzed fenamiphos on nine different packed columns[13]. Various detectors were used for GC analysis. Ripley *et al.* worked with Ni-ECD and NP-TID detectors[45]; NPD was suitably applied in water analysis[42]; FPD and electrolytic conductivity detectors[16] were also applied. Three reports were found concerning GC-MS analysis[11,40,46], one of these for water analysis, using an ion trap detector in the Cl mode[40]. Cl pulsed positive/negative SIM detection[11] and EI ionization were reported[46] but not for water analysis.

HPLC analysis: A reversed phase column was successfully used by Di Corcia *et al.*[41] employing an UV detector. Various post column photolysis reaction detectors—fluorimetric, electrochemical and conductivity—are reported[39,47]. Two reports were found on the use of HPLC-MS, and a TSP interface was utilized for water analysis of fenamiphos[44].

Oxydemeton-methyl

22 papers were found; of these 17 on GC and three on HPLC, but not one concerning water analysis of oxydemeton-methyl. We found one article where oxydemeton-methyl was analyzed by TLC[48].

GC analysis: Split and splitless injection were mainly used[4,11] with SE54, SE30 and OV101 capillary columns. FID, employing an OV101 packed column[4], FPD and electrolytic conductivity detectors[20] are reported, and three used GC-MS analysis. EI ionization was the most frequent[46], also in SIM[23] while one study reported CI pulsed positive/negative detection in SIM for oxydemeton-methyl, trichlorfon, fenamiphos and other organophosphorus pesticides[11]. Greenhalgh *et al.*[49] trifluoroacethylated oxydemeton-methyl and others compounds containing the sulfoxide moiety before GC analysis.

HPLC analysis: Reversed-phase was used[30,31] and the electrolytic conductivity detector was employed by Dolan *et al.*[50].

Benazolin

Only one report was found on the analysis of this pesticide[51] and it was performed by GC in split injection and using a DB-1 capillary column. Derivatization was necessary with (2-cyanoethyl)dimethyl(diethylamino)silane and the kinetics of the reaction was studied. At room temperature reaction was complete within minutes and the derivatization product was stable for more than 36 hours. NPD and MS were used.

Maneb

We found 13 reports, 8 on GC and 6 on HPLC analysis (one considered both the techniques), but no papers were found on water analysis.

GC analysis: GC analysis of maneb and other dithiocarbamates is currently based on carbon disulfide determination by acidic hydrolysis and headspace GC analysis[52,53]. McGhie *et al.*[53] analyzed maneb by carbon disulfide determination using a packed column with 4% QF1 plus 1% OV17 or with SE30, and a FPD, while Jongen *et al.*[52] used a CpSil8 capillary column with the ECD.

HPLC analysis: Maneb and other dithiocarbamates were analyzed using reversed-phase HPLC (RP18) after derivatization with methyl iodide using an UV detector[54]. Methylation was performed on the free dithiocarbamic acid, obtained from dithiocarbamate pesticide with EDTA, using methyl iodide in the transfer phase reaction. Post-column reaction detection was also used[55].

Metham sodium salt

Nine reports were found on the analysis of metham sodium salt. One report was on GC analysis, but only of methyl isothiocyanate formed from this pesticide[56], while the others dealt with HPLC analysis. In two cases water was analyzed[57,58]. Mullins *et al.*[57] analyzed metham sodium and the related methyl isothiocyanate in pond water and sewage effluent using direct injection with an automatic loop; recovery was more than 92%.

HPLC analysis: Some authors have used a micellar mobile phase[57,59] or transition metal salts as ion pair reagents[60]. Different detector have been employed beside UV, particularly the diode array detector[58] and fluorometric detection after post-column photolysis[61]. No reports were found on HPLC-MS.

Metham acid

One report was found on the analysis of this pesticide. Moriyasu *et al.*[62] analyzed aliphatic amines by HPLC after conversion to dithiocarbamate chelates of Ni(II), Pd(II) and Hg(II). A Lichrosorb Si 100 column and UV detection were used.

Ziram

We found 13 reports, five on GC and eight on HPLC analysis. Only one article was on water analysis[63].

GC analysis: As for other dithiocarbamate pesticides, GC analysis is based on determination of carbon disulfide by headspace injector[64]. Krupcik *et al.* analyzed ziram and other dithiocarbamic metal complexes of Zn(II) and Ni(II) as intact product using a glass capillary column and SE30 and OV101 as stationary phase, with a FID[65]. They discuss the synthesis and MS analysis (with the direct inlet system) of these dithiocarbamic complexes.

HPLC analysis: Reversed phase was commonly used for ziram and other dithiocarbamates (metham sodium salt and maneb were analized with this technique) after derivatization with methyl iodide and employing the UV detector[54], while other authors analyzed ziram and other zinc dithiocarbamates after conversion to the corresponding cobalt (III) complexes[66]. Ibrahim *et al.*[67] used both reversed and normal phase microcolumns for HPLC analysis with plasma emission detection using a glass frit nebulizer interface. One paper was found on HPLC-MS analysis of ziram in water, and a particle beam interface was used[63].

Phenmedipham

Thirty reports were found on the analysis of phenmedipham, eight by GC and 21 by HPLC. Seven studies dealth with water analysis[68–71]. Agostiano *et al.*[71] analyzed phenmedipham by HPTLC with quantification by fluorescence densitometer, and obtained 94% recovery after extraction with Tenax resin from water at 1 μg/l. Crathorne *et al.*[70] used XAD-2 resin and HPLC with UV diode array detector, and off-line MS and MS/MS identification was obtained by field desorption and fast atom bombardment.

GC analysis: The main problem for GC analysis of this and other carbamate pesticides is their decomposition into the corresponding isocyanate. Saxton[4] published the GC analysis of phenmedipham by injection at 150°C, using a packed column with 5% OV101 and FID, but he did not specify whether this decomposition occurred. Stan *et al.*[72] analyzed this pesticide, and other carbamates, after derivatization with trifluoroacetyl anhydride, to obtain the corresponding phenol ester. They used split-splitess injection and a capillary column coated with HP1 stationary phase, with MS by EI ionization in positive ion recording and NPD as the detection modes.

HPLC analysis: Reversed-phase was commonly adopted[61], either using a gradient elution[73] or working in direct liquid introduction[74]. Normally UV detection was used directly[68] or after post-column photolysis for fluorometric determination[61], but Von Nehring *et al.* employed an electrochemical detector[75]. Six reports were on HPLC and MS analysis of phenmedipham[69,70,74,76] (one with field desorption mass spectrometry, but not coupled with HPLC[69]).

Trichloroacetic acid (TCA)

We found 77 reports, but many were not pertinent, because TCA is frequently used as ion pair reagent or as precipitating agent for proteins. However, 44 papers were found for GC

and six for HPLC analysis of this pesticide, including 11 on water analysis[77–83]. Ozawa *et al.*[78] studied recovery from water, using Dowex 1-X8 and Dowex VGR resins, at different NaCl concentrations in the eluent and, using the second resin, they obtained 99% recovery with 1.5 molar NaCl in the eluent, from natural water at 10 μg/l. TCA was also analyzed as a by-product of humic acid in chlorinated waters[80,83].

GC analysis: Head-space injection is widely used, but chloroform deriving from TCA thermal decomposition is analyzed by this technique, using a ECD[84,85]. For intact TCA splitless injection is currently used[78,86,87] and columns packed with 10% Carbowax 20[86] or Supelco GP[88] phases, or capillary columns[87,89], with SE30 or OV351 as phases. ECD[78,87,88] and FID[86,89] were the most frequent, but the plasma emission detector was used for water analysis by GC with a procedure of precolumn trap enrichement[82].

Three reports were found on the use of mass spectrometry coupled with GC[77,80,90]. Interestingly, Braun[90] analyzed TCA as the methyl ester obtained by treatment with diazomethane, by GC-MS CI-positive SIM technique, considering TCA as resulting from perchloroethylene metabolism. As in the latter case, TCA is frequently analyzed as the methyl ester obtained by simple treatment with diazomethane[88,90], but C_1-C_8 aliphatic monochloroalkyl esters[89], pentafluorobenzylation[87] and derivatization with difluoroanilide[78] have also been considered.

HPLC analysis: Reversed phase was widely employed, using iron(II)-1 10-phenanthroline complex as mobile phase additive[91] or ion pair and ion exchange phases, compared by Stevens *et al.*[92]; an amino column was also used[93]. The UV detector was the most widely used in HPLC analysis of TCA. Tsuchiya *et al.*[94] used fluorescence detection after reaction with 4-bromoethyl-7-acetoxycoumarin.

CONCLUSIONS

We present the results of a library search based on a Chemical Abstracts report. For some pesticides we found methods that successfully analyzed water samples at the required limit of detection. Various GC or HPLC methods were found, that can probably be adapted to water sample analysis. For a few of the pesticides considered analysis will require more extensive study.

Acknowledgements

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