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Review

Chromatographic analysis of chemical warfare agents

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CONTENTS

1. INTRODUCTION

Chemical weapons continue to be used in armed conflicts[1], although various treaties have been or are being negotiated[2]. Hence adequate analytical methods are required that would allow verification that treaties on the prohibition of chemical weapons are observed[3–5]. In this respect, a research project has been established in Finland on the identification and determination of over 100 warfare agents and 86 products of their degradation[6–16], and a study of this and related problems has been

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made by a group of Canadian researchers on the order of the Secretary General of UNO[17].

The problems connected with the determination of substances classified as potential warfare agents lie also in the non-military sphere of interest. This concerns, for instance, the uncontrolled spread of toxic substances as a result of industrial breakdown or agrotechnical operations, and the generation of poisons, *e.g.*, fluoroacetic acid in plants or phosgene in the troposphere[18–20].

The detection and determination of highly toxic substances in complex environmental and biological systems by conventional chemical and biochemical methods is difficult and time-consuming, and the results are often dubious. These methods are now being systematically replaced by instrumental analytical methods, among which chromatographic procedures play an important role. The latter are distinguished by their high detectability, rapidity and the possibility of operation in a continuous mode. Chromatographic methods allow the isolation of analytes from complex matrices and their identification and determination even at picogram levels.

The number of publications on the determination of chemical warfare agents by chromatographic methods is considerable, but none of the chromatographic systems is universal, as they do not allow the analysis of all compounds simultaneously and under the same conditions. This is to be expected, as the main property that allows the classification of a substance as a warfare agent is its toxicity and applicability on the battle field[21]. The various chemical warfare agents differ considerably in their physico-chemical properties, *e.g.*, polarity and boiling point, which are decesive for chromatographic separations. The problems connected with the selection of chromatographic systems become even more complicated as it is necessary also to take into account the degradation of warfare agents, the starting materials used for their synthesis and contaminants.

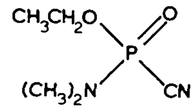
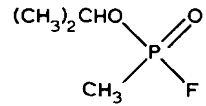
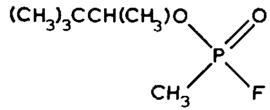
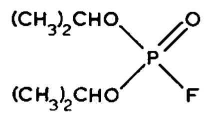
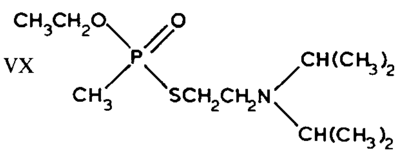
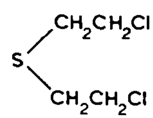
Hitherto several surveys have been published on the applications of chromatography in the analysis of chemical warfare agents, but their approach was superficial[4,22,23]. In this review, an attempt is made to survey comprehensively the possibilities of applying modern chromatographic methods in the analysis of chemical warfare agents. We therefore consider thin-layer chromatography (TLC), gas chromatography (GC), and high-performance liquid chromatography (HPLC), and survey their applications in the analysis of the following types of chemical warfare agents: organophosphorus [tabun (GA), sarin (GB), soman (GD), DFP and VX]; vesicants [mustard gas (HD), nitrogen mustard (HN-3) and lewisite (L)]; irritants [2-bromobenzylnitrile (CA), 2-chloroacetophenone (CN), dibenz[*b, f*]-1,4-oxazepine (CR), *o*-chlorobenzylidenemalononitrile (CS), adamsite (DM) and chloropicrin (PS)]; psychotoxic [3-quinuclidinylbenzylate (BZ)]; and industrial [cyanogen chloride (CK), hydrocyanic acid (AC), phosgene (CG), fluoroacetic acid and sodium fluoroacetate]. The formulae and physico-chemical properties of these substances are given in Table 1.

2. METHODS OF COLLECTING AND PREPARING SAMPLES OF CHEMICAL WARFARE AGENTS FOR ANALYSIS

A sample after collection should have a composition representative of that of the original contaminated material, *i.e.*, the quantitative proportions of the components in the collected sample and in the initial bulk material should be identical.

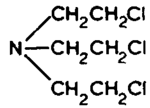
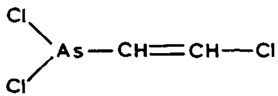
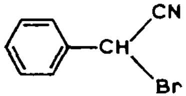
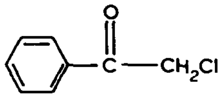
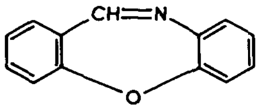
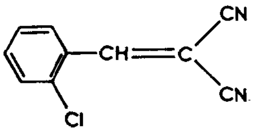
TABLE 1

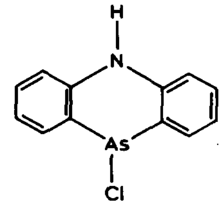
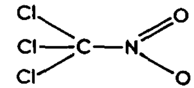
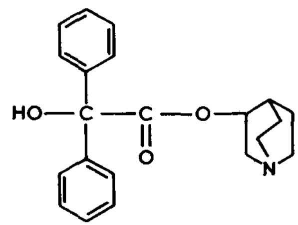
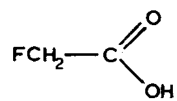
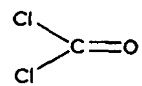
SELECTED PHYSICO-CHEMICAL PROPERTIES OF CHEMICAL WARFARE AGENTS

Chemical name	*Common name*	*Abbreviation*[a]	*Structure*	*Molecular weight*	*m.p. (°C)*	*b.p. (°C)*	*Ref.*
Ethyl N,N′-dimethylphosphoroamidocyanidate	Tabun	GA		162.1	−50	230[b]	24
Isopropyl methylphosphonofluoridate	Sarin	GB		140.1	−54	151.5[b]	24
Pinacolyl methylphosphonofluoridate	Soman	GD		182.1	−80	167[b]	24
Diisopropyl phosphorofluoridate	DFP	PF-3		184.2	−82	183[b]	11
O-Ethyl, S-2-diisopropylaminoethyl methylphosphonothiolate	VX	VX		267.3	−30	>300[b]	24
Bis(2-chloroethyl)sulphide	Mustard gas yperite	HD		159.1	14.5	217[b]	24

(*Continued on p. 296*)

TABLE I (*continued*)

Chemical name	*Common name*	*Abbreviation*[a]	*Structure*	*Molecular weight*	*m.p. (°C)*	*b.p. (°C)*	*Ref.*
Tris(2-chloroethyl)amine	Nitrogen gas	HN-3		204.5	−4	235[b]	24
2-Chlorovinyldichloroarsine	Lewisite[c]	L		207.3	−2.4	196.6[b]	24
2-Bromobenzylnitrile	Camite	CA		196.0	25	242[b]	24
2-Chloroacetophenone		CN		154.5	59	245	24
Dibenz[*b*,*f*]-1,4-oxazepine		CR		195.2	71–72	300	24
2-Chlorobenzylidenemalonodinitrile		CS		188.6	95–96	310–315	11

10-Chloro-5,10-dihydrophenarsazine	Adamsite	DM		277.5	195	410	24
Trichloronitromethane	Chloropicrin	PS		164.4	−64	112.3	24
3-Quinuclidinylbenzylate		BZ		337.4	164–165	320	24
Fluoroacetic acid		—		78.0	33	167	25
Hydrocyanic acid		AC	HCN	27.0	−13.3	25.7	24
Cyanogen chloride		CK	ClCN	61.5	−6.9	12.6	24
Carbonyl chloride	Phosgene	CG		98.9	−118	8.2	24

[a]Notation used in U.S. Army.
[b]Degradation of compound.
[c]Data for *trans* isomer.

The chromatographic separation proper is usually preceded by the isolation of the substances to be determined from a sample collected directly from the environment[26]. Application of sensitive selective detectors often allows some stages of preparation of the sample to be omitted, but even very small amounts of contaminants may sometimes occur that make an acceptable determination difficult or even impossible. It is often necessary to subject the toxic substances to be determined to repeated concentration[27].

A method that allows the isolation of the substance to be analysed from the condensed (liquid or solid) matrix is the headspace procedure[28–31], which consists in analysing the vapour phase of substances in thermodynamic equilibrium with the same substances in the condensed phase. There are two modifications of the method. In the first, vapour (*e.g.*, of chloropicrin[32]) is collected from over the condensate placed in a closed vessel after phase equilibrium has been established. The second modification consists in passing an inert gas over the condensed phase, vapour of the analyte being entrained and subsequently analysed chromatographically. The dynamic modification has a higher sensitivity and, when the system is kept under constant conditions, the concentration of the component to be determined varies almost linearly with the volume of the inert gas passed, which facilitates quantitative analysis. This procedure has been used to isolate certain chemical warfare agents that decomposed in the first modification (*e.g.*, soman[9]).

To accelerate the establishment of equilibrium in the system in the headspace method, the temperature is increased, the liquid phase is salted-out or the surface of the condensed phase is expanded. The headspace technique may be used to determine substances whose boiling points lie in a wide range, *e.g.*, from 26°C (HCN) to 178°C (methylheptanol)[33].

The vapour from over the condensed phase may be analysed directly after it has been introduced in an adequate volume into the chromatographic column. One can also arrange that the sample from the equilibrium vessel is introduced into the chromatographic column with a cooled section where the sample components undergo sorption on the stationary phase; their separation starts when cooling is discontinued.

Much attention has been devoted to sample preparation for chromatographic analysis and new devices and instrumentation have been designed for this purpose[34]. Nevertheless, a survey of methods for collecting samples of materials contaminated with chemical warfare agents shows that no universal method exists. The choice of a method depends on the kind of agent and contaminated material, and also on the purpose of the analysis. The problems of the reliability of the results of the analysis of toxic compounds related to the collection of samples have been discussed in the literature[4,6,9,10,35–37]. The methods of isolating chemical warfare agents from various media are given below in greater detail.

2.1. Air

Sample collection of chemical warfare agents from air is carried out mainly by absorption and adsorption methods[38,39], which make possible the simultaneous concentration of the compounds to be analysed.

Absorption methods consist in passing contaminated air through a solvent, mixture of solvents or solution in which the toxic compound dissolves, sometimes with the formation of its derivatives[40–43]. By applying solvents with a high boiling point with good absorption of the analyte substances, trace amounts of warfare agents present in air can be concentrated. To increase the efficiency of absorption of lower boiling components, cooling of the sorption system with ice, dry-ice or liquified gases is often applied[13,44]. The solution of the toxic substance obtained as a result of absorption is often suitable for direct use in chromatographic analysis.

If it is necessary for the measurements proper to be preceded by additional concentration of trace amounts of the toxic agent to a level corresponding to the sensitivity of the measuring system, then, depending on the physico-chemical properties of the substances being analysed, distillation or extraction is applied[45]. Distillation is usually used when the sample contains components that differ considerably in volatility, whereas extraction is applied when the components have similar volatilities but different solubilities.

Distillation permits the separation of volatile organic substances from the non-volatile residue. To reduce the effects connected with the chemical derivatization of the compounds to be analysed (due to heating), distillation is sometimes conducted in a stream of inert gas and under reduced pressure. The volatile components are collected in adsorption columns or condensed in receivers[46,47].

Extraction consists in washing the dissolved sample with small volumes of a solvent selected so that it be immiscible with the sample solvent and that the partition coefficients of the components being analysed be higher than those of the matrix components. If necessary, the extract obtained is concentrated by evaporation of the solvent, sometimes in an inert gas (*e.g.*, nitrogen) atmosphere[9,32,48].

Adsorption is the fundamental technique used in the collection of samples of the substances to be analysed from air[6,9,10,49]. This process is carried out in samplers filled with adsorbents such as active carbon, silica gel, Tenax GC, porous polymers (Porapak Q and N, Chromosorb 102), XAD resins (XAD-1, -2, -4, -7) or polyurethane foam. Most of these materials are used as fillings of chromatographic columns[50–56]. Note that it is not recommended to use active carbon for the adsorption of organophosphorus compounds as it may induce their decomposition[9]. To concentrate a mixture whose components differ significantly in volatility, complex systems are used, composed of layers of different adsorbents, *e.g.*, polyurethane foam and XAD-2[13], Ambesorb, Chromosorb[104] and Tenax GC[56], or samplers filled with a mixture of adsorbents[57–59].

Air humidity may hinder significantly the process of sorption on the adsorbent, so various drying agents (*e.g.*, magnesium perchlorate) are used. They are placed directly before the adsorption sampler[48,60].

The chemical warfare agents are transferred from the adsorbent to the liquid or gas phase by applying extraction in the liquid–solid system or thermal desorption[52].

Extraction is the most common method of transferring the chemical warfare agents from the adsorbent into solution. Its advantage is the possibility of obtaining concentrated components in liquid form suitable for direct analysis by any chromatographic procedure (GC, HPLC, TLC).

Thermal desorption of the components trapped on the adsorbent is used when analysis is carried out by GC. This method allows almost 100% recovery of the adsorbed, thermally stable compounds[61], and the detectable concentrations of chemical warfare agents are 2–3 orders of magnitude lower than when extraction is used[56]. Tenax GC, characterized by a high thermal stability (up to 375°C) and resistance to hydrolysis, proved to be the best sorbent for application in the desorption technique[9,56]. When the boiling temperatures of the sample components differ substantially, it may be necessary to separate them by desorption and repeated adsorption of the more volatile components. The desorption of these components is conducted for 10–15 min in a stream of inert (carrier) gas, then they are adsorbed in an adsorption column preceding the gas chromatograph column or trapped in few initial cooled coils of the capillary chromatographic column. The subsequent rapid (several dozen seconds) heating of these intermediate traps makes it possible to introduce the sample into the main column without producing excessive diffusion of the peak fronts of the chromatographed substances[62–66].

In the analysis of chemical warfare agents, it is not recommended to use glass or metal vessels for contaminated air samples, as irreversible adsorption of these agents on the vessel walls or even their decomposition may occur. The use of inert materials such as PTFE or polyethylene is to be preferred[67].

Aerosols are collected on filter-paper or other filters with suitable pore diameters[68]. From the military point of view, the most important is the aerosol fraction with particles of diameter not exceeding 5 μm, as this fraction has the ability to remain suspended for long periods in the layers of air close to the earth's surface. An assembly for the two-step isolation of chemical warfare agents from air has been presented[10]. In this assembly the aerosols are arrested on a Whatman GF/A glass-fibre filter and the gases and vapours in an adsorption column filled with XAD-2 resin or active carbon. This assembly was used for collecting air samples from an aircraft[69].

In the West-German MM-1 field gas chromatograph combined with a mass spectrometer, the sample is concentrated with the help of selective silicone membranes[70]. The latter adsorb organic pollutants from air, allowing the simultaneous diffusion of chemical warfare agents into the chromatographic column. The diffusion is accelerated by heating the membrane. This procedure is also used in the analysis of water pollutants.

2.2. Water

In water analysis, the dissolved chemical warfare agents are isolated mainly by extraction or adsorption[71,72] methods or by a combination of both[73]. Less frequently, although to an increasing extent, the headspace method is also used.

For extraction, commonly available solvents are usually used[74–78]. In order to increase the partition coefficients of the substances being extracted between the two liquid phases, neutral salts are often added[79,80], *e.g.*, for the extraction of organophosphorus compounds[77].

In the adsorption method, columns are used filled usually with XAD-2, -4 or -7 resin[81,82]. The structure of these resins allows the sorption of organic compounds in the micropores without offering a greater resistance to water flow. The adsorption of the toxic agent is the greater the higher is its molecular weight and the greater its hydrophobicity. The kind of the resin used depends on the polarity of the compound being isolated. It has been shown that XAD-2 resin can be used for the quantitative isolation from water of many classes of compounds at concentrations ranging from 10^{-5} to 10^{-6}%. For pesticides, present in water at a concentration of the order of 10^{-10}%, the recovery achieved was 80–95%[56]. For most chemical warfare agents it is suggested that XAD-4 resin is used[9,10]. Adsorptive materials such as Porapak, Tenax

GC, μBondapak C_{18}, polyurethane foams and graphitized carbon black are also used[56,83–85].

In order to enrich samples containing trace amounts of the analysed components, lyophilisation is sometimes applied. For this purpose a salt, *e.g.*, sodium chloride, is added to the water being analysed and the system is subjected to freezing. Next water is removed by sublimation of ice. The residue contains the salt and the chemical warfare agents.

In a different procedure, an organic solvent is added to the water and, after freezing out ice, the organic phase is removed. This method of enriching the sample is suitable for treating solutions of concentrations lower than 0.01 mol/l. At higher concentrations losses of the component being determined may occur due to its occlusion on the forming ice[36].

It is often advantageous to subject the sample components to chemical derivatization prior to their isolation. Owing to the presence in their molecules of polar groups and their high molecular weights, many organic compounds are of low volatility and on heating undergo thermal decomposition or intramolecular rearrangement. By derivatization such as acetylation, methylation, perfluoroacetylation or silylation one can increase the volatility of the compounds and, as a result, facilitate their chromatographic analysis. An exhaustive survey of methods for the derivatization of compounds prior to their chromatographic analysis was made by Blau and King[86].

An interesting concept of combining extraction and derivatization in one process was advanced by Rosenfeld *et al.*[87]. XAD-2 resin impregnated with benzyl or pentafluorobenzyl bromide was used. The impregnants caused derivatization of the organic acids adsorbed from water. It seems that this method could be used successfully in the analysis of decomposition products of organophosphorus compounds by gas or liquid chromatography.

2.3. *Soil*

Most methods of collecting samples of soil are fairly complex. In principle, they are useful only with respect to chemically stable chemical warfare agents which are resistant to degradation reactions caused by the influence of the environment[88,89]. The most common method of isolating the compounds to be analysed from soil is their extraction with organic solvents, preceded by preliminary wetting of the soil with water[90,91].

De Leeuw *et al.*[92] described a method of isolating volatile and medium volatile substances from soil. It consists in direct evaporation of the substances to be analysed in a pyrolyser by means of a metal wire which is heated rapidly (0.1–0.2 s). The compounds liberated due to heating or generated in the course of pyrolysis are passed through a capillary column in which they are separated. Good reproducibility of results of analysis was achieved with this method.

Some chemical warfare agents present in soil may be analysed by the headspace technique.

2.4. *Vegetable material*

In phytochemical analysis, the residues of toxic substances are usually isolated by simple methods. In most instances the sample is homogenized and the components to be analysed are extracted in a Soxhlet apparatus with a mixture of organic solvents[90,93–100]. The extract obtained is usually dried, *e.g.*, with sodium sulphate, and filtered through a Whatman filter-paper.

If the samples contain wax in amounts greater than 15%, the latter is removed preliminarily by treating the sample with a non-polar solvent or, depending on the sample composition, the components to be analysed are isolated without removing the wax by using more polar solvents, *e.g.*, a mixture of acetonitrile, benzene and hexane[101].

To ensure a better separation of the contaminants from the compounds being determined, the extract obtained is passed through a column filled with active carbon, aluminium oxide or Celite[102,103]. The process of separation of the components of interest from the contaminants extracted with them is controlled by selection of a suitable adsorbent. For this purpose thin-layer chromatography may also be used[93,94].

2.5. Samples for determining the contamination of humans and animals

The degree of contamination of humans and animals is usually assessed by analysing body fluids such as blood, plasma or urine. The concentration of a chemical warfare agent in blood and plasma is representative of the mean concentration of that agent in the whole organism. In contrast, samples of urine sometimes show significant differences in the concentration of the chemical warfare agents being determined from those actually found in the contaminated organism. The isolation of the components to be determined from the body fluids is usually effected by extraction, *e.g.*, with dichloromethane, diethyl ether, *n*-hexane or ethyl acetate[104–111]. The extract obtained may subsequently be purified in columns filled with Sep-Pak C_{18} or on plates coated with silica gel and then extracted again[112–115].

In the analysis of biological samples, the headspace technique may also be used. It has been applied, for instance, for the isolation of hydrogen cyanide from blood[116,117] and of mustard gas from urine[118,119]. Chemical derivatization of the sample components may also be used for the isolation of chemical warfare agents from biological matter[120]. If tissue is the sample material, it is extracted, after homogenizing, with water and the aqueous extract is concentrated[121,122].

A scheme of the procedure for the chromatographic analysis of various materials contaminated with chemical warfare agents is given in Fig. 1. The choice of a suitable chromatographic technique depends on several factors: availability of apparatus, professional training of personnel, conditions under which the analysis is to be carried out, time allowed for the analysis and purpose for which the results are designed (qualitative, semi-quantitative, quantitative) and their accuracy. Consideration of these factors, and the number of publications involving different techniques, indicate that today the most useful for the analysis of chemical warfare agents is GC, TLC and particularly HPLC being of lesser importance.

3. ANALYSIS OF CHEMICAL WARFARE AGENTS BY THIN-LAYER CHROMATOGRAPHY

3.1. General

TLC is widely used in many analyses, including routine qualitative, semi-quantitative and quantitative applications. The present state of art of TLC, which has been very well described by Geiss[123], shows development along three main lines: devel-

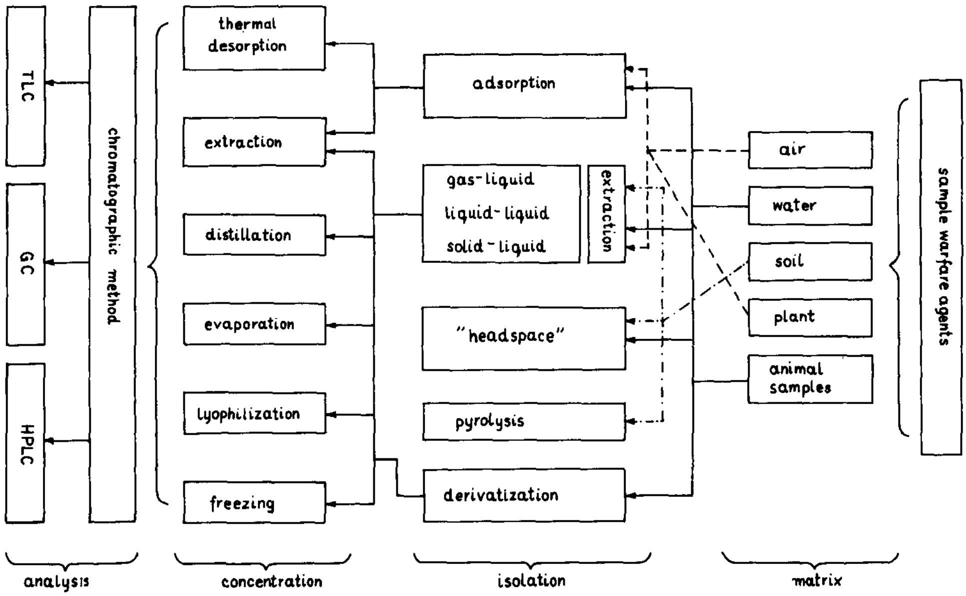


Fig. 1. Scheme for sample preparation of different materials contaminated with chemical warfare agents.

opment of new chromatographic chambers distinguished by their higher separating efficiency and shorter times of developing *e.g.*, overpressured TLC (OPTLC)[124–130] or the Soczewinski chamber[131,132], seeking new materials for the thin layers in high-performance TLC (HPTLC)[133,134]; and seeking new methods for detection and better interpretation of chromatograms[135–137].

The high selectivity, high detectability and reliability of analysis under fairly simple conditions contribute to the effective use of TLC for the detection of most chemical warfare agents in both fixed and mobile (field) laboratories. If the chemical warfare agents are to be determined in a sample of unknown provenance, and it is necessary to repeat many times the separation and identification of the sample components under various conditions, then the TLC method is very useful.

Application of TLC for military purposes, including analytical procedures for chemical warfare agents, has been recommended by many workers[6,7,138,139]. In a report prepared by the Ministry of Foreign Affairs in Finland, the use of TLC for detecting chemical warfare agents on the battlefield is recommended and it is instructed that it be included in the outfit of a mobile laboratory[6]. TLC is one of the basic methods used in some armies for the detection of chemical warefare agents under field conditions.

The adsorbent used as the stationary phase has less influence than the mobile phase on the course and results of analysis carried out by TLC[140]. Most commonly silica gel is used in the analysis of chemical warfare agents. Aluminium oxide is used to a much lesser extent, and reports of the use of cellulose or polyamide are exceptional. The selection of a suitable developing system with an adequate eluting capacity ensures the required separation of a sample mixture[141].

The basis for the identification of a chemical warfare agent is the location of its spot on the chromatogram, which can be expressed in quantitative terms by the R_F value. Accurate identification in this way requires a highly selective developing system and accurate observance of the prescribed conditions regarding the kind of chromatographic chamber, plate, developing system and temperature. However, if we take advantage of the additional information as to the colour of the spot, which is revealed by spraying the plate with a selective detection reagent, then a proper identification may be possible even without accurate observation of the specified conditions. The limit of detection of chemical warfare agents by TLC and common colour reactions is 10^{-6}–10^{-9} of the compound in the spot.

3.2. *Organophosphorus compounds*

Organophosphorus chemical warfare agents were discovered shortly before World War II and have been intensively investigated ever since. The earliest group of compounds obtained are denoted by the letter G; those obtained later are more toxic and bear the symbol V (VX, VN). All organophosphorus agents are lethal, their action consisting in the inhibitive blocking of cholinesterase. If we take advantage of this enzymatic reaction for visualizing thin-layer chromatograms, very good detection of organophosphorus compounds is achieved[142,143]. McKinley and co-workers[144,145] were the first to apply the enzyme inhibition reaction in chromatographic analysis in the early 1960s and subsequently the same group[146,147] created the foundations of modern enzymatic analysis. Ever since, many papers have been published[148–151], and also surveys[152], on the determination of organophosphorus pesticides and other enzyme inhibitors. The detection limit of the inhibitor being analysed depends on its origin and on the conditions and time of storage of the enzyme, and lies in the range 10^{-9}–10^{-12} g of the inhibitor in the spot[99,138,151].

An example of the application of the enzymatic method to the detection and identification of organophosphorus agents was described by Stachlewska-Wróblowa[138]. She sprayed the plate with an aqueous solution of the enzyme and then with a mixture of 2-naphthol acetate and diazotized *o*-dianisidine in aqueous alcohol. At the sites where organophosphorus compounds were present white spots appeared on the intensely violet background of the plate. This method of detection made it possible to detect 10 ng of the substance in the spot. With VN_1 two spots were obtained, which was ascribed to the presence of two isomers, thiol and thionic. She also used indoxyl acetate and its derivatives as detection reagents. As a result of enzymatic hydrolysis, fluorescent indoxyl was formed at the sites where the enzyme inhibitor was absent. Dark, non-fluorescent spots on a bluish green background visible under UV light made it possible to detect sarin and soman in amount of 5 ng per spot.

The presence of other inhibitors of enzymes in samples of chemical warfare agents complicates TLC with enzymatic detection, although it is still possible, which was shown by distinguishing organophosphorus pesticides and carbamates blocking cholinesterase from warfare agents[153]. Five selective detection reactions were applied, which made possible the identification of ten insecticides, soman and VX. The total time of analysis did not exceed 30 min.

Analysis of the chromatograms of organophosphorus compounds of the VX type containing a ternary nitrogen atom in the molecule and separated on silica gel plates showed that these compounds usually remain at the start owing to the formation of salts on the slightly acidic surface of the adsorbent. It was possible to eliminate this effect by adding to the mobile phase a small amount of a base, *e.g.*, diethylamine[154]. It is not desirable to adopt this approach when analysing complex mixtures of chemical warfare agents as some of them, *e.g.*, sarin, react with the amine to give amides.

DFP can be well detected without resort to the enzymatic reaction. Jacobson and Patchornik[155] studied the possibility of detecting DFP by using coloured nitrophenols and nitrothiophenols, which are electrophilic reagents. The highest detectability of DFP was achieved when 2,4-dinitrothiophenol (DNPS) and 2,4,6-trinitrothiophenol (TNPS) were used. The brown (DNPS) or orange (TNPS) spot was visible for several minutes, after which it became decolorized. The spot became coloured again after it was sprayed with a solution of sodium hydroxide. The detection reaction was tested on various plates, *e.g.*, with silica gel, cellulose or polyamide, and in all instances similar results were obtained. The high detectability (1–2 nmol in the spot) was stated to be due to the hydrolysis of DFP and formation of fluoride ion. Stachlewska-Wróblowa[156] described the analysis of a mixture of twelve compounds (organophosphorus, necrotic and irritant compounds). The detection of organophosphorus chemical warfare agents by the enzymatic method was hindered by the appearance of yellow spots due to CS and chloroacetophenone and, when iodine activation was applied, also spots due to adamsite appeared. In order to achieve complete identification of the particular compounds, analysis was conducted in two chromatographic systems. In the first, the mobile phase was *n*-hexane – dioxane – pyridine. The spots were detected using the enzymatic reaction (spots of sarin, soman, tabun, VN_1, CS and CN appeared) and Rhodamine B and Tollens reagent (spots of HD, CA, CS, CN and DM appeared). The separation of the irritants (CS, CN and DM) from the organophosphorus compounds (sarin, tabun) was carried out with a mobile phase consisting of dichloroethane and ethyl acetate. The spots were revealed by the enzymatic method. Preliminary spraying of the plate with a solution of iodine in chloroform improved the contours of the spots and made possible the detection of adamsite.

A mixture containing sarin, soman and VX with six other chemical warfare agents was chromatographed in normal and pressure chromatographic chambers. The chromatograms obtained were similar, although the R_F values using the pressure chamber were higher. For example, the R_F value for soman in the pressure chamber was 0.7 and in the normal saturated chamber 0.38. The chromatogram development time in the pressure chamber was much shorter than that in the normal chamber.

3.3. Vesicant compounds

Vesicant (blistering) warfare agents act locally on the body surface giving symptoms similar to scorches with necrosis of the tissue. They also exert a toxic effect on the whole organism which may lead to death. Among necrotic compounds, mustard gas [bis (2-chloroethyl) sulphide] is the most important; it was used first during World War I, so its chemical analysis is well developed.

Today many types of sulphur and nitrogen yperites are known. Their analysis, especially in multi-component mixtures, by conventional chemical methods is difficult, whereas it is fairly easy by chromatographic methods. A mixture of sulphur and nitrogen yperites was separated by Sass and Stutz[107]. They used as the group reagent 4-(4′-nitrobenzyl)pyridine, which gave a blue spot with all yperites. The compounds belonging to the sulphur or nitrogen yperite group with similar R_F values were detected with various agents. This made it possible to distinguish 1,2-bis(2-chloroethyl) thioloethane (Q) from 2,2′,2″-trichlorotriethylamine (HN-3), for which the R_F values were 0.68 and 0.66, respectively. The detection limit for Q was two orders of magnitude lower than that for HN-3. In general, yperites were determined at the microgram level.

Mustard gas was also determined in a mixture containing organophosphorus and/or organochlorine insecticides[158]. The identification of mustard gas was possible owing to the use of a solvent in which mustard gas has a high R_F value and the remaining components a low value or by detection of the spot with a selective reagent, *e.g.*, iodoplatinate (PtI_6^{2-}). The sensitivity of the reaction allowed the detection of mustard gas at the submicrogram level.

Munavalli and Pannella[159] analysed mustard gas and its metabolites in biological fluids, testing fifteen developing systems. For detection a solution of potassium permanganate and sodium carbonate was used, which yielded yellow spots on a pink background. The spots were stable for many hours. It was also found that the chromatograms can be detected with a solution of 4-(4′-nitrobenzyl)pyridine in acetone.

Heating of the plate and its exposure to the action of ammonia vapour developed blue spots of mustard gas. The latter method allows mustard gas to be detected in an amount of about 0.056 μg in 1 cm^3 of solution.

The above methods of analysing yperites by TLC with the use of chemical reactions for detection make it possible to detect and determine yperites present in microgram amounts. Similar possibilities exist when a biochemical reaction is used for the detection of mustard gas on the chromatograms[160]. Mustard gas may be determined quantitatively on the thin-layer chromatogram several hours after development. By measuring the radioactivity of mustard gas labelled with ^{35}S it was shown that the losses of mustard gas in chromatograms stored for 24 h do not exceed 5%[161].

A survey of the applications of paper, thin-layer and gas chromatographic methods for detecting alkylating agents, and also sulphur and nitrogen yperites, was published by Fishbein and Falk[162].

Vesicant warfare agents also include organic arsines. However, in view of their lesser importance, many fewer examples of their analysis have been reported. Stachlewska-Wróblowa analysed primary, secondary and tertiary organic arsines[163,164].

3.4. Irritants

The irritant agents include lachrymators and sternites. These agents are not lethal but by acting on the eyes (lachrymators) and on the respiratory tract (sternites) they hinder normal functioning. This group of agents include substances that differ considerably in chemical structure, which makes their analysis fairly difficult. This is due to, among other things, the large differences in their polarity. Ludemann *et al.*[165] drew attention to this fact when analysing irritant agents and the contaminants commonly present in them. They described the use of plates with different adsorbents, different developing systems and various detection agents in the analysis of bromobenzyl cyanide, *o*-chlorobenzalmalononitrile, chloroacetophenone and diphenylaminochloroarsine. Under optimum conditions it was possible to detect 1 μg or even less of the agent. A similar detectability of irritants was also achieved by other workers[138,166,167].

TABLE 2

EXAMPLES OF ANALYSIS OF CHEMICAL WARFARE AGENTS BY TLC

Chemical warfare agent	*TLC plate*	*Mobile phase*	*Detection reagent*	R_F	*Ref.*
Organophosphorus compounds					
GA	Silica gel 60–Kieselguhr F_{254} (Merck 5567)	*n*-Hexane–pyridine–dioxane (7:2:1)	ChE solution–β-naphtol acetate + *o*-dianisidine	0.48	138, 156
		n-Hexane–pyridine (4:1)		0.36	156
		Dichloroethane–ethyl acetate (7:3)	ChE solution–β-naphthol acetate + *o*-dianisidine	0.54	156
		n-Hexane–acetone–pyridine (7:1:2)	ChE solution–β-naphthol acetate + *o*-dianisidine	0.55	156
	Silica gel	Dichloromethane		0.05	6
		Acetone		0.60	6
		n-Heptane–acetone (3:2)		0.00	6
		Chloroform–methanol (4:1)		0.73	6
		n-Hexane–acetone–dichloromethane (7:2:1)	5% NaOH + 1% H_2O_2–cobalt(III) chloride solution	0.26	154
GB	Silica gel 60–Kieselguhr F_{254} (Merck 5567)	*n*-Hexane–pyridine–dioxane (7:2:1)	ChE solution–β-naphthol acetate + *o*-dianisidine	0.57	138, 156
		n-Hexane–pyridine (4:1)		0.48	156
		Dichloroethane–ethyl acetate (7:3)	ChE solution–β-naphthol acetate + *o*-dianisidine	0.44	156

(Continued on p. 308)

TABLE 2 (*continued*)

Chemical warfare agent	*TLC plate*	*Mobile phase*	*Detection reagent*	R_F	*Ref.*
	Silica gel	*n*-Heptane–acetone (3:2)		0.17	6
		Chloroform–methanol (4:1)		0.76	6
		Dichloromethane		0.05	6
		Acetone		0.63	6
		n-Hexane–acetone–dichloromethane (7:2:1)		0.27	154
	Silica gel (Merck 5562)	Acetone–carbon tetrachloride (1:4)	ChE solution–IBCh solution + Michler's hydrol	0.48	157
GD	Silica gel 60–Kieselguhr F_{254} (Merck 5567)	*n*-Hexane–pyridine–dioxane (7:2:1)	ChE solution–*β*-naphthol acetate + *o*-dianisidine	0.67	138, 156
		Dichloroethane–ethyl acetate (9:1)	Aldehyde reagent	0.42	153
		Ethyl acetate	Aldehyde reagent	0.95	153
		Dichloroethane	Aldehyde reagent	0.14	153
		n-Hexane–pyridine (4:1)		0.59	156
		n-Hexane–acetone–pyridine (7:1:2)	ChE solution–*β*-naphthol acetate + *o*-dianisidine	0.70	156
		Dichloroethane–ethyl acetate (7:3)	ChE solution–*β*-naphthol acetate + *o*-dianisidine	0.62	156
	Silica gel	*n*-Hexane–acetone–dichloromethane (7:2:1)	5% NaOH + 1% H_2O_2–cobalt(III) chloride solution	0.41	154
	Silica gel (Merck 5562)	Acetone–carbon tetrachloride (1:4)	ChE solution–IBCh solution + Michler's hydrol	0.70	157

DFP	Silica gel	Dichloromethane		0.10	6
		n-Heptane–acetone (3:2)		0.33	6
		Acetone		0.67	6
		Chloroform–methanol (4:1)		0.75	6
		n-Hexane–acetone–dichloromethane (7:2:1)	5% NaOH + 1% H_2O_2–cobalt (III) chloride solution	0.50	154
VX	Silica gel 60–Kieselguhr F_{254} (Merck 5567)	*n*-Hexane–pyridine–dioxane (7:2:1)	ChE solution–β-naphthol acetate + *o*-dianisidine or 0.5% iodine solution	0.05 0.18	138, 156
		Dichloroethane–ethyl acetate (9:1)	0.5% Iodine solution or 0.5% $KMnO_4$ solution	<0.06	153
		Ethyl acetate	0.5% Iodine solution or 0.5% $KMnO_4$ solution	<0.15	153
		Dichloroethane	0.5% Iodine solution or 0.5% $KMnO_4$ solution	<0.08	153
		Benzene–*n*-hexane (3:1)	Rhodamine B–Tollens reagent–UV	0.00	156
		n-Hexane–pyridine (4:1)		0.10	156
		n-Hexane–acetone–pyridine (7:1:2)	Rhodamine B–Tollens reagent–UV or ChE solution–β-naphthol acetate + *o*-dianisidine	0.21	156
	Silica gel (Merck 5562)	Acetone–carbon tetrachloride (4:1)	ChE solution–IBCh solution + Michler's hydrol	0.03	157
	Alumina gel (Merck 5575)	Benzene–acetic acid (4:1)	0.5% Iodine solution	0.64	156
Vesicant compounds					
HD	Silica gel 60–Kieselguhr F_{254} (Merck 5567)	*n*-Hexane–pyridine–dioxane (7:2:1)	Rhodamine B–Tollens reagent–UV	0.71	138, 156
		Benzene–*n*-hexane (3:1)	Rhodamine B–Tollens reagent–UV	0.72	156

(*Continued on p. 310*)

TABLE 2 (*continued*)

Chemical warfare agent	*TLC plate*	*Mobile phase*	*Detection reagent*	R_F	*Ref.*
		n-Hexane–acetone–pyridine (7:2:1)	Rhodamine B–Tollens reagent–UV	0.75	156
	Silica gel	*n*-Hexane–acetone (7:3)		0.57	6
		Dichloromethane		0.65	6
		Chloroform–methanol (4:1)		0.72	6
		Dichloromethane	4-(4′-Nitrobenzyl)pyridine–5% sodium perchlorate–piperidine or *o*-dianisidine solution–copper(II) acetate–96% H_2SO_4	0.77	107
	Silica gel 60 F_{254}	Dichloromethane	Palladium chloride solution	0.77	114
	Silica gel (Merck 5721)	Benzene–chloroform (1:1)		0.79	156
		Benzene–acetic acid (9:1)		0.88	156
	Silica gel (Merck 5562)	Acetone–carbon tetrachloride (1:4)	Michler's ketone + mercury(I) chloride solution	0.67	157
	Silica gel	Dichloromethane–*n*-hexane (1:1)	Iodoplatinate solution $[PtI_6]^{2-}$ or Michler's ketone + mercury bromide or silver nitrate–UV or triphenylmethane solution + silver nitrate or selenic acid	>0.80	158
	Silica gel GF	Chloroform–acetone (5:4)	4-(4′-Nitrobenzyl)pyridine or 1% $KMnO_4$ solution	0.89	159
		Acetonitrile–ethanol (10:1)	4-(4′-Nitrobenzyl)pyridine or 1% $KMnO_4$ solution	0.92	159
		Acetonitrile	4-(4′-Nitrobenzyl)pyridine or 1% $KMnO_4$ solution	0.96	159

	Silica gel GF or HPTLC GHLF or Whatman LHP-KF	Chloroform–methanol (10:1)	4-(4′-Nitrobenzyl)pyridine or 1% $KMnO_4$ solution	0.94	159
		Chloroform–acetonitrile (5:1)	4-(4′-Nitrobenzyl)pyridine	0.95	159
	Silica gel G	Chloroform–acetone (5:4)	Radiation detector	0.80	161
	Alumina gel (Merck 5575)	Benzene–acetic acid (4:1)	Tollens reagent–UV	0.87	156
HN-3	Silica gel	*n*-Hexane–acetone (7:3)		0.50	6
		Dichloromethane		0.55	6
		Chloroform–methanol (4:1)		0.78	6
	Silica gel G	Dichloromethane	4-(4′-Nitrobenzyl)pyridine–5% sodium perchlorate–piperidine or *o*-dianisidine solution–copper(II) acetate–96% H_2SO_4	0.66	107
L	Silica gel	*n*-Hexane–acetone (7:3)		0.00	6
		Dichloromethane		0.00	6
		Chloroform–methanol (4:1)		0.58	6
	Silica gel (Merck 5562)	Acetone–carbon tetrachloride (1:4)	Michler's thioketone–formalin + 96% H_2SO_4	0.00	157
	Silica gel (Merck 5553 or Merck 5748)	Benzene–acetic acid–2-propanol (17:1:2)	Bromocresol purple solution–25% ammonia or dithizone–acetic acid or 0.1% iodine solution or Michler's thioketone solution	0.19	163, 164
Irritant compounds					
CA	Silica gel 60–Kieselguhr F_{254} (Merck 5567)	*n*-Hexane–pyridine–dioxane (7:2:1)	Rhodamine B–Tollens reagent–UV	0.59	138, 156

(*Continued on p. 312*)

TABLE 2 (*continued*)

Chemical warfare agent	*TLC plate*	*Mobile phase*	*Detection reagent*	R_F	*Ref.*
		Benzene–*n*-hexane (3:1)	Rhodamine B–Tollens reagent–UV	0.60	156
	Silica gel	Toluene–dichloroethane (1:1)	Thiocarbamide–*o*-dianisidine or Michler's thioketone solution	0.51	138
	Silica gel (Merck 5721)	Benzene–chloroform (1:1)		0.67	156
		Benzene–acetic acid (9:1)		0.72	156
	Silica gel G	Benzene	4-(4'-Nitrobenzyl)pyridine–5% sodium perchlorate–piperidine	0.52	165
	Alumina gel (Merck 5575)	Benzene–acetic acid (4:1)	Tollens reagent–UV	0.87	156
	Acid alumina gel	Dichloromethane–benzene (1:3)	4-(4'-Nitrobenzyl)pyridine–5% sodium perchlorate–piperidine or iodine	0.58	165
		Chloroform–benzene (1:19)	Quinone solution or quinone + 5% NaOH or 4-(4'-nitrobenzyl)pyridine–5% sodium perchlorate–piperidine	0.65	165
CN	Silica gel 60–Kieselguhr F_{254} (Merck 5567)	*n*-Hexane–pyridine–dioxane (7:2:1)	ChE solution–β-naphthol acetate + *o*-dianisidine or Rhodamine B–Tollens reagent–UV	0.57	138, 156
		Benzene–*n*-hexane (3:1)	Rhodamine B–Tollens reagent–UV	0.44	156
		n-Hexane–acetone–pyridine (7:1:2)	Rhodamine B–Tollens reagent–UV or ChE solution –β-naphthol acetate + *o*-dianisidine or benzofurazan oxide + 1 *M* NaOH or thiocarbamide solution + *o*-dianisidine	0.63	156

		Dichloroethane–ethyl acetate (7:3)	ChE solution–β-naphthol acetate + *o*-dianisidine	0.78	156
	Silica gel	*n*-Hexane–acetone (7:3)		0.47	6
		Dichloromethane		0.57	6
		Toluene–dichloroethane (1:1)	Thiocarbamide–*o*-dianisidine or Michler's thioketone solution	0.36	138
	Silica gel (Merck 5721)	Benzene–chloroform (1:1)		0.48	156
		Benzene–acetic acid (9:1)		0.50	156
	Silica gel (Merck 5562)	Acetone–carbon tetrachloride (1:4)	*m*-Dinitrobenzene–5 *M* KOH	0.69	157
	Silica gel (Merck 5553)	Chloroform	*m*-Dinitrobenzene + benzofurazan oxide–5 *M* KOH or $KMnO_4$ solution	0.41	168
	Alumina gel (Merck 5575)	Benzene–acetic acid (4:1)	Tollens reagent–UV	0.87	156
	Acid alumina gel	Dichloromethane–benzene (1:3)	Iodine or 4-(4'-nitrobenzyl)pyridine–5% sodium perchlorate–piperidine	0.45	165
		Chloroform–benzene (1:19)	Quinone solution–5% NaOH or 4-(4'-nitrobenzyl) pyridine–5% sodium perchlorate–piperidine	0.50	165
CR	Silica gel	Dichloromethane		0.10	6
		n-Hexane–acetone (7:3)		0.37	6
	Silica gel (Merck 5553)	Chloroform	Dragendorff's reagent or $KMnO_4$ solution	0.12	168
CS	Silica gel 60–Kieselguhr F_{254} (Merck 5567)	*n*-Hexane–pyridine–dioxane (7:2:1)	ChE solution–β-naphthol acetate + *o*-dianisidine or Rhodamine B–Tollens reagent–UV	0.57	138, 156

(Continued on p. 314)

TABLE 2 (*continued*)

Chemical warfare agent	*TLC plate*	*Mobile phase*	*Detection reagent*	R_F	*Ref.*
		Benzene–*n*-hexane (3:1)	Rhodamine B–Tollens reagent–UV	0.48	156
		n-Hexane–acetone–pyridine (7:1:2)	Rhodamine B–UV or ChE solution–β-naphthol acetate + *o*-dianisidine or benzofurazan oxide + 1*M* NaOH	0.63	156
		Dichloroethane–ethyl acetate (7:3)	ChE solution–β-naphthol acetate + *o*-dianisidine	0.78	156
	Silica gel	*n*-Hexane –acetone (7:3)		0.43	6
		Dichloromethane		0.60	6
		Toluene–dichloroethane (1:1)	Thiocarbamide–*o*-dianisidine or Michler's thioketone solution	0.43	138
	Silica gel (Merck 5721)	Benzene–chloroform (1:1)		0.53	156
		Benzene–acetic acid (9:1)		0.56	156
	Silica gel (Merck 5562)	Acetone–carbon tetrachloride (1:4)	*m*-Dinitrobenzene–5 *M* KOH	0.67	157
	Silica gel (Merck 5721)	Chloroform	*m*-Dinitrobenzene + benzofurazan oxide–5 *M* KOH or $KMnO_4$ solution	0.45	168
	Alumina gel (Merck 5575)	Benzene–acetic acid (4:1)	Tollens reagent–UV	0.87	156
	Acid alumina gel	Dichloromethane–benzene (1:3)	Iodine or 4-(4'nitrobenzyl)pyridine–5% sodium perchlorate–piperidine	0.53	165

		Chloroform–benzene (1:19)	Quinone solution or quinone + 5% NaOH or 4-(4′ nitrobenzyl)pyridine–5% sodium perchlorate–piperidine	0.55	165
DM	Silica gel 60–Kieselguhr F_{254} (Merck 5567)	*n*-Hexane–pyridine–dioxane (7:2:1)	Rhodamine B–Tollens reagent or 0.5% iodine solution	0.24	138, 156
		Benzene–*n*-hexane (3:1)	Rhodamine B–Tollens reagent	0.00	156
		n-Hexane–acetone–pyridine (7:1:2)	Rhodamine B–UV	0.28	156
		Dichloroethane–ethyl acetate (7:3)	Iodine solution–ChE solution–*β*-naphthol acetate + *o*-dianisidine	0.29	156
	Silica gel (Merck 5721)	Dichloromethane–2-propanol–ethyl acetate (2:1:1)		0.79	156
	Silica gel (Merck 5562)	Acetone–carbon tetrachloride (1:4)	Michler's thioketone–formalin + 96% H_2SO_4	0.37	157
	Silica gel (Merck 5553 or 5748)	Benzene–acetic acid–2-propanol (17:1:2)	Bromocresol purple solution–25% ammonia or dithizone–acetic acid or 0.1% iodine solution or Michler's thioketone solution	0.47	163, 164
	Basic silica gel G	Ethyl acetate–methanol (1:9)	*o*-Dianisidine–copper(II) acetate–50% H_2SO_4	0.23	165
	Silica gel G	Acetone–chloroform (1:4)	*o*-Dianisidine–copper(II) acetate–50% H_2SO_4	0.35	165
	Alumina gel (Merck 5575)	Benzene–acetic acid (4:1)	Iodine solution or Tollens reagent–UV	0.72	156
	Acid alumina gel	Chloroform–benzene (1:19)	*o*-Dianisidine–copper(II) acetate–50% H_2SO_4	0.00	165
Psychotoxic compound					
BZ	Silica gel	Acetone–carbon tetrachloride (1:4)	Formalin + 96% H_2SO_4	0.06	157

Dibenzo[*b,f*]-1,4-oxazepine (CR) was analysed in the presence of *o*-chlorobenzalmalononitrile and chloroacetophenone by Rosłonek *et al.*[168]. Good separations were obtained when chloroform was used as the eluent and Dragendorff reagent as a specific detection reagent for CR. The detection limit of CR was 0.2 mg/cm^3. The presence of other chemical warfare agents in the mixture had no effect on the elution and identification of the irritants.

In Table 2, examples are given of the analysis of chemical warfare agents by TLC.

4. ANALYSIS OF CHEMICAL WARFARE AGENTS BY HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY

4.1. General

Theoretically, all chemical warfare agents analysed by TLC can also be analysed by HPLC. The practical difficulty consists, however, in the lack of a suitable detector for some of these substances. Mostly in HPLC, detectors are used in which advantage is taken of UV absorption by the compounds being detected. The use of such detectors is therefore limited to compounds that contain chromophore groups active in the UV region or to those wich can easily be converted into compounds with such groups. UV-detection allows the analysis of irritants and analogous phytotoxic compounds at the nanogram level. Most chemical warfare agents, however, do not show absorption in the UV region or the absorption is very weak, and their conversion to UV-active derivatives complicates the analysis.

Fluorescence and electrochemical detectors are also used in HPLC. A typical fluorescence detector is about 1000 times more sensitive than a UV detector. The use of such a detector is, however, limited to fluorescent compounds or compounds that can easily be converted into such. Hence fluorescence detectors find very limited application in analysis of chemical warfare agents. The applicability of electrochemical detectors in such analyses is even more restricted.

Other types of detection system not commonly used but finding application in HPLC might also be used in the analysis of chemical warfare agents and their analogues, *e.g.* flame ionization detection (FID)[169] and flame photometric detection (FPD)[170,171]. Spectroscopic methods have also been used, *e.g.*, mass spectrometry (MS)[172–175], Fourier transformation IR (FT-IR)[8] and ion-mobility spectrometry[176–179]. Good results were obtained by applying nuclear magnetic resonance (NMR)[8], and also a detection system taking advantage of the transformations of the chemical substance eluted from the column[180]. In the analysis of organophosphorus agents, detection involving the use of enzymatic reactions is particularly desirable[9–13,181]. Using this detection method it is possible to determine organophosphorus compounds at the picogram level.

In HPLC, non-polar stationary phases chemically bonded to the substrate are today chiefly used as column fillings; these are fillings for reversed-phase chromatography. They allow the analysis of complex mixtures containing, as is often the case with chemical warfare agents, compounds with different functional groups. For the separation of chemical warfare agents, standard stainless-steel columns are used, filled with, *e.g.*, LiChrosorb Hibar RP-18, Spherisorb S5 ODS-2 or Zorbax ODS. The advantages of these stationary phases are their resistance to the destructive action of eluents of different pH, the possibility of introducing aqueous samples directly into the chromatographic column and the relatively rapid establishment of thermodynamic equilibrium of the chromatographic system.

In accordance with the general properties of HPLC, the quality of separation of chemical warfare agents depends on the composition of the eluent. In most instances good results are obtained by applying isocratic chromatography, although sometimes, especially when the mixture is very complex (organophosphorus agents in the presence of HD, CS, DM and its hydrolysis product and BZ), it is recommended to apply gradient chromatography[12,55,182]. In most commonly used types of reversed-phase chromatography the eluent usually includes water and methanol or acetonitrile.

The identification of chemical warfare agents separated in the chromatographic column can be made on the basis of the retention indices relative to a selected homologous series[183–185]. For instance, for the identification of irritants or psychotoxins, use is made of the alkyl aryl ketone and 1-*p*-(2,3-dihydroxypropyloxy)phenylalkanone homologous series[186].

4.2. Examples

For organophosphorus chemical warfare agents the enzymatic method of detection is the most appropriate in view of the required detectability. It takes advantage of the inhibition of the enzyme by the organophosphorus compound. The non-inhibited enzyme decomposes certain chemical compounds (substrates), *e.g.*, butyrylcholine iodide. As a result, the pH of the solution changes, producing a change in colour of an added acid–base indicator. After inhibition the enzyme has a lower ability to decompose the substrate, so the pH of the medium is less affected and the colour of the indicator changes more slowly or does not change at all. Usually only part of the eluate from the column is introduced into the reaction vessel, and the effect of the reaction is determined spectrophotometrically[55,187]. A schematic diagram and an example of enzymatic detection in HPLC are shown in Fig. 2.

One of the problems involved in enzymatic detection is the composition of the eluent. Enzymatic reactions proceed best in aqueous solutions, and certain organic solvents affect the course of these reactions very negatively. For instance, acetonitrile is less useful than methanol as a component of the eluent[55]. The results of analysis obtained also depend on the kind of enzyme used. This is shown in Fig. 3 for acetylcholinesterases obtained from an electric eel and from human serum. Acetylthiocholine iodide was used as the substrate in this reaction and 5,5-dithiobis(2-nitrobenzoic acid) as the colour reagent[55]. The detection limit achieved for sarin and soman was 10 pg and for tabun 60 pg.

The enzymatic detector not only reveals the presence in the sample of organophosphorus agents but also indicates the presence of other inhibitors of enzymes such as organophosphorus pesticides and carbamates. The analysis of chemical warfare agents in the presence of other inhibitors may be difficult if their separation is incomplete. This problem may be solved, however, by applying additionally a UV detector sensitive only to compounds posessing chromophore groups (which is the case with most pesticides).

Analysis of organophosphorus agents with the help of HPLC can also be carried out by derivatization to introduce a chromophore or fluorescent substituent into

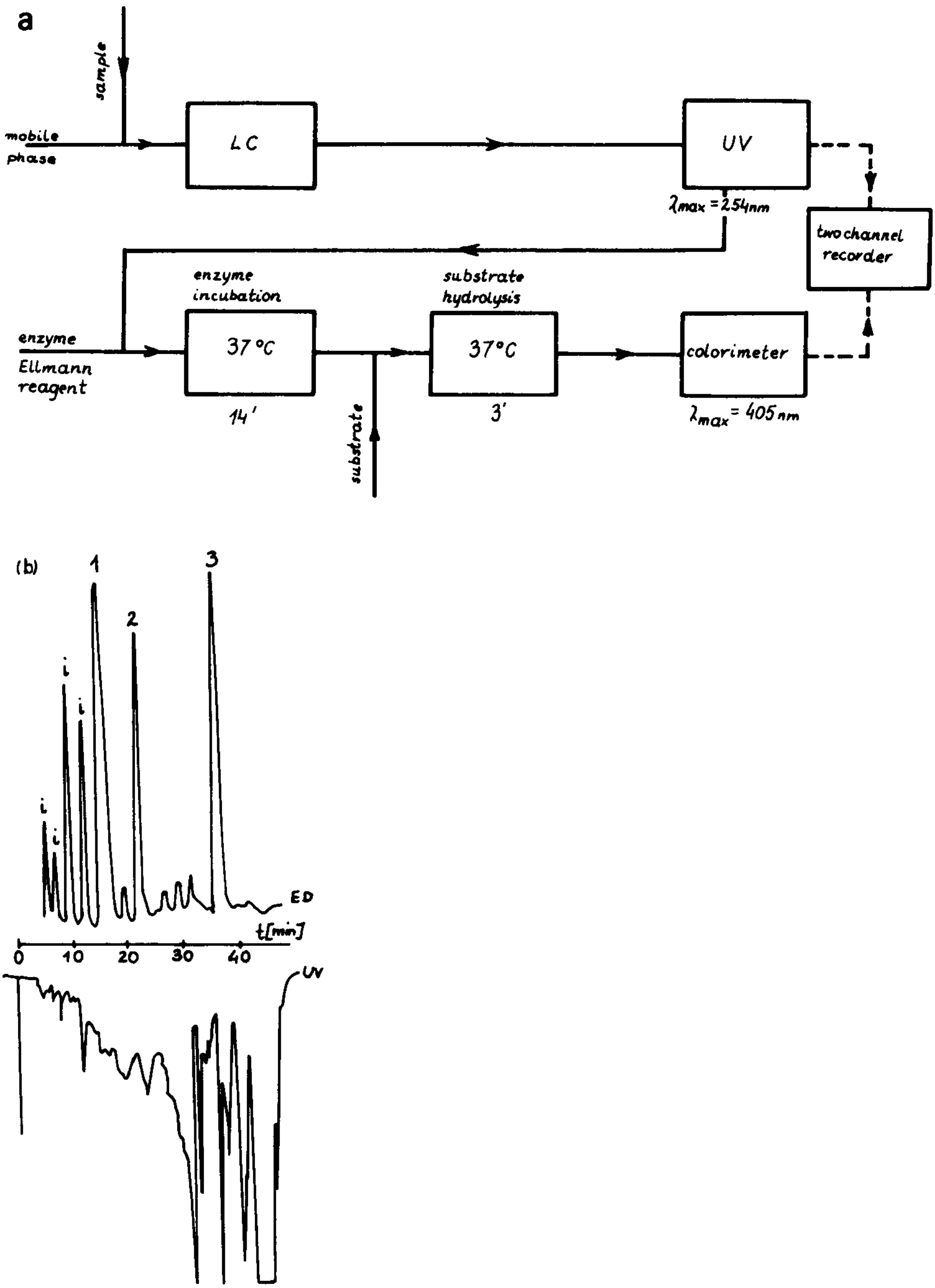


Fig. 2. (a) Scheme of the HPLC–UV enzymatic detection system for analysis of air contaminated with phosphorus chemical warfare agents and (b) the chromatogram obtained with the system. i = Impurities; 1 = sarin; 2 = tabun; 3 = soman. Conditions: 250 mm × 4.0 mm I.D. column with 5-μm LiChrosorb RP-18; linear gradient, 15–65% methanol in water in 35 min; flow-rate, 0.7 ml/min; enzymatic detection with human serum ChE[55].

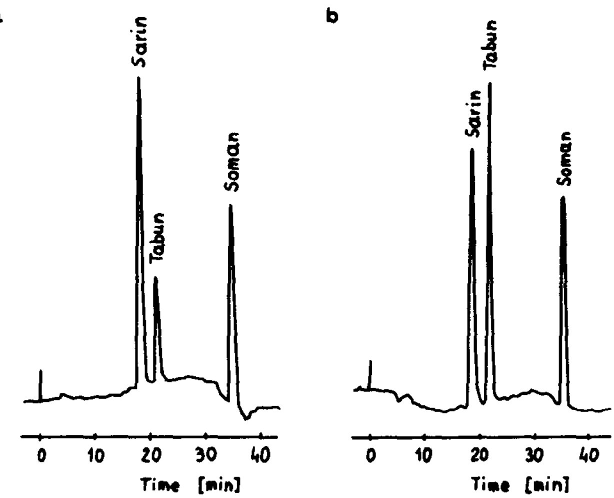


Fig. 3. Chromatogram of sarin, soman and tabun in acetone obtained by using (a) electric eel AChE and (b) human serum ChE. Conditions: 250 mm × 4.0 mm I.D. column with 5-μm LiChrosorb RP-18; linear gradient, 15–65% methanol in water in 35 min; flow-rate, 0.7 ml/min[55].

the molecule. This method was applied to identify the products of hydrolysis of organophosphorus agents after their reaction with pentafluorobenzyl bromide[8]. By applying this procedure it was possible not only to use a UV detector but sometimes also to achieve a better chromatographic separation when the detectability of the chromatographed substances was good.

By using octadecylsilane as the stationary phase, methanol–water as the mobile phase and a UV detector it was possible to obtain good results in the analysis of irritant mixtures[9–11]. For detecting particular species it is recommended to take measurements at the following wavelengths[13,186]: DM (hydrolysis products), 224, 282; CS, 220, 254, 280, 300; CN, 254 and CR, 280, 313 nm. These substances can be detected at nanogram levels, the retention times being moderate and the reproducibility of the results of analysis good.

Analysis by reversed-phase chromatography of three common irritants showed that in methanol CR tends to decompose so a special technique of mixing the solvents had to be applied[188]. The results of analysis of irritants in samples of vegetable origin are usually inferior to those obtained for other samples[189]. An example of the separation of irritants is shown in Fig. 4.

Bossle *et al.*[190] determined vesicant compounds (2-chloroethyl sulphide and the products of its decomposition) after having converted them by reaction with chloramine B sodium salt into products revealing strong absorption in the UV region. The absorption maximum was observed at 254 nm. The chromatographic separations were carried out on a column filled with Radial-Pak C_{18} with water–acetone as the mobile phase. It was claimed that under these conditions it is also possible to analyse mustard gas.

Reversed-phase HPLC gives good results with organoarsenic compounds. The difficult and sometimes even impossible analysis of these compounds by GC is fairly easy using HPLC[191,192].

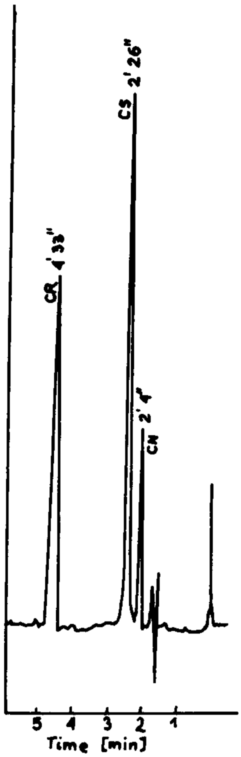


Fig. 4. Separation of CN, CR and CS by reversed-phase HPLC. Conditions: column with μBondapak C_{18}; mobile phase, methanol–water (7:3); flow-rate, 2 ml/min; detection, UV (280 nm); amounts, CN = 40 ng, CR = 30 ng, CS = 24 ng[188].

Among the analyses of other toxic substances, the determination of sodium fluoroacetate deserves some attention. Collins *et al.*[193] adapted the method proposed by Lam and Grushka[194] for separating fluorescent derivatives of monocarboxylic acids obtained by reaction with 4-bromomethyl-7-methoxycoumarin, using a fluorescence detector.

For the HPLC analysis of sodium fluoroacetate use was also made of the reaction with *p*-bromophenacyl bromide[121] or with *o,p*-nitrobenzyl-N,N'-diisopropylisourea[122]. This made possible the determination of sodium fluoroacetate by means of a UV detector.

The determination of phosgene by HPLC as described by Hori *et al.*[195] is worth considering. Phosgene was determined in the products of combustion of vinyl chloride by passing them through a solution of aniline.

Some chemical warfare agents may be used to analyse other organic compounds by HPLC. Someno *et al.*[196] presented a sensitive and specific method for determining the activity of two types of urokinase in human urine after their reaction with [^{3}H]DFP. The latter compound reacted selectively with urokinase to yield stable complexes. The complexes of the particular types of urokinase were separated in a chromatographic column. The eluate from the column was mixed with a liquid scintillating agent and the radioactivity was measured with a detector.

The derivatization reaction with the use of phosgene may be very useful for the HPLC separation of enantiomers of various compounds yielding oxazolidones with phosgene. A detailed description of such procedures was given in the survey by Gyllenhaal and Vessman[197].

Some examples of the analysis of chemical warfare agents by HPLC are given in Table 3.

5. ANALYSIS OF CHEMICAL WARFARE AGENTS BY GAS CHROMATOGRAPHY

5.1. *General*

GC is a convenient method for analysis of complex mixtures as it allows the identification and determination of particular components. As with other organic compounds, the analysis of chemical warfare agents is possible if their vapour pressure is sufficiently high or if they can be brought into the gaseous state without decomposition or with accurately repeatable decomposition. Almost all chemical warfare agents comply with these requirements. So far, attempts to apply GC to the analysis of chemical warfare agents has failed in only a few instances which concerned chiefly arsenic compounds[10].

Initially in the analysis of chemical warfare agents by GC, packed glass or metal columns were chiefly used. For analysing compounds of high reactivity, *e.g.*, phosgene, columns made of inert materials, *e.g.*, PTFE, were used[198].

In the analysis of chemical warfare agents which are mostly polar, the choice of a suitable support, especially when trace analysis is involved, is of primary importance[199]. Hence, most often neutral silanized supports are used, chiefly Chromosorb G and W and Gas-Chrom Q and P[100,104,105,200–203]. Packed columns are being replaced to an increasing extent by capillary columns, especially the fused-silica type[6,204–207]. The availability of these columns is connected with progress in fibre-optic technology. Fused-silica capillary columns coated on the outside with polyimide or aluminium show very good mechanical strength. The inner diameter of capillary columns ranges from 0.1 to 0.75 mm. Their separating efficiency is better than that of packed columns, the time of separation is short and the peaks obtained are symmetrical.

The samples may be injected into capillary columns in different ways. One of the better solutions is that in which the sample is introduced into the column directly[208]. This method has been applied successfully in the analysis of chemical warfare agents[9,10,91] and organophosphorus pesticides[209]. A disadvantage of this method of introducing the sample into the column is the possibility of the column becoming contaminated, which may lead to a decrease in its efficiency. Despite this, the superiority of the direct method has been confirmed[210]. By direct injection of the sample into the columnn, partial or complete thermal decomposition of some compounds (*e.g.*, VX) is avoided as the necessity to evaporate the analyte substances in the injector is eliminated. Another advantage of direct injection of samples is the high accuracy of determination (2–4%) and rapid elution of the well developed peaks with good stability of the baseline[8].

A widely used procedure for injecting samples into capillary columns is that with splitting of the carrier gas stream[211]. In the analysis of chemical warfare agents, the splitting ratio of the gas stream is usually 1:10. It should be borne in mind that in

TABLE 3

EXAMPLES OF ANALYSIS OF CHEMICAL WARFARE AGENTS BY HPLC

Chemical warfare agent	*Column characteristics*	*Detection*	λ_{max} *(nm)*	*Detection limit*	*Remarks*	*Ref.*
BZ CS CN	Octadecyl silane stationary phase, mobile phase, 50% methanol–water to 100% methanol	UV	254	<1 ng (CN)	Separation from phenoxyacetic acids	10
GB GD DFP-3	250 mm x 4.6 mm I.D., 10-μm C_9 Spherisorb or 5-μm Spherisorb S 5 ODS 2; 250 mm x 4.0 mm I.D., 5-μm LiChrosorb Hibar RP-18; mobile phase, 50% methanol–water or 50% methanol–phosphate buffer	UV–enzymatic	254	3.3 ng (GB) 1.2 ng (GD) 747 ng (DFP-3)		11
DM	250 mm x 4.6 mm I.D., 10-μm C_9 Spherisorb or 5-μm Spherisorb S 5 ODS 2; 250 mm x 4.0 mm I.D., 5-μm LiChrosorb Hibar RP-18; mobile phase, 50% methanol–water to 100% methanol, 50°C	UV	282	<1 ng	Analysis of degradation products of DM	11
BZ CS HD	250 mm x 9.4 mm I.D., 10-μm Zorbax-ODS, mobile phase, 50% methanol–water to 100% methanol, 50°C	UV	220 254 280 300		Identification and determination of chemical warfare agents in a complex mixture using single-step HPLC separation	13
GA GB GD		Enzymatic				

BZ CN CR CS DM	250 mm x 4.0 mm I.D., 5-μm LiChrosorb Hibar RP-18; mobile phase, 50% methanol–water to 100% methanol, 50°C	UV	220 254 280 300	ng	Determination of retention indices	13, 186
GA GB GD	250 mm x 4.0 mm I.D., 5-μm LiChrosorb RP-18; mobile phase, 15% methanol–water to 65% methanol–water	UV–enzymatic	254	10 pg (GB) 10 pg (GD) 60 pg (GA)	Analysis of urban air samples	55, 181
FCH_2COONa	10-μm octadecylsilane stationary phase	UV	254 280	1–50 ppm	Determination in canine gastric content after derivatization with *o,p*-nitrobenzyl-N,N′-diisopropylisourea	122
CN CR CS	μBondapak C_{18}; mobile phase, ethanol–water (7:3)	UV	254 280 313	<1 ng	Trace-level detection in the range 1–10 ng	188
FCH_2COOH	250 mm x 4.0 mm I.D., Lichrosorb RP-8; mobile phase, acetonitrile–water (1:2) or ethyl acetate–acetonitrile–water (9:2:22)	FD	360 ex. 400 em. 410 em.	0.2 ng per 100 ml	Determination in poison baits; separation of C_1–C_3 carboxylic acids	193
CG	500 mm x 4.0 mm I.D., divinylbenzene–styrene copolymer stationary phase; mobile phase, methanol–water (9:1)	UV	254	0.55 ppm	Determination in combustion gases of vinyl chloride monomer after derivatization in aniline solution	195

the analysis of some organosphosphorus agents (*e.g.*, soman), strong adsorption on the active surface of the glass injector occurs. This limits significantly the detectability of the compounds being determined[9]. Hydrogen cyanide and phosgene also are strongly adsorbed or undergo decomposition, which results in additional ghost peaks on the chromatogram. These unfavourable effects are eliminated by periodic cleaning, acid deactivation or silanization of the injection system.

When using GC for the analysis of chemical warfare agents, a universal stationary phase is sought that permits the effective separation of the greatest possible number of these compounds. In the report of the Finnish Ministry of Foreign Affairs[10], it is stated that among about a dozen stationary phases tested, SE-52 and OV-1 show properties nearest to those required. These phases have high thermal stability and do not react with the chemical warfare agents. Among other phases suitable for the separation of psychotoxic agents, OV-210, Emulphor ON-870, Triton X-305, Silar 10C and FFAP are recommended[22]. SE-54, DB-5 and FFAP are recommended for use in the analysis of organophosphorus compounds, vesicants and irritants[8,13]. OV-1701 was used for analysing DFP and SE-54 for hydrogen cyanide, cyanogen chloride and phosgene[10].

Four stationary phases, DB-1, DB-5, DB-1701 and DB WAX, in the order of increasing polarity, were tested and it was found that the first three may be used for the simultaneous chromatography of most chemical warfare agents and similar compounds[91]. An example of the separation of mixture of such compounds is shown in Fig. 5.

The principal aim of the analysis of chemical warfare agents is the identification of an unknown toxic substance in the sample. This is usually done by comparing the retention indices of the substance being analysed those of a standard measured in at

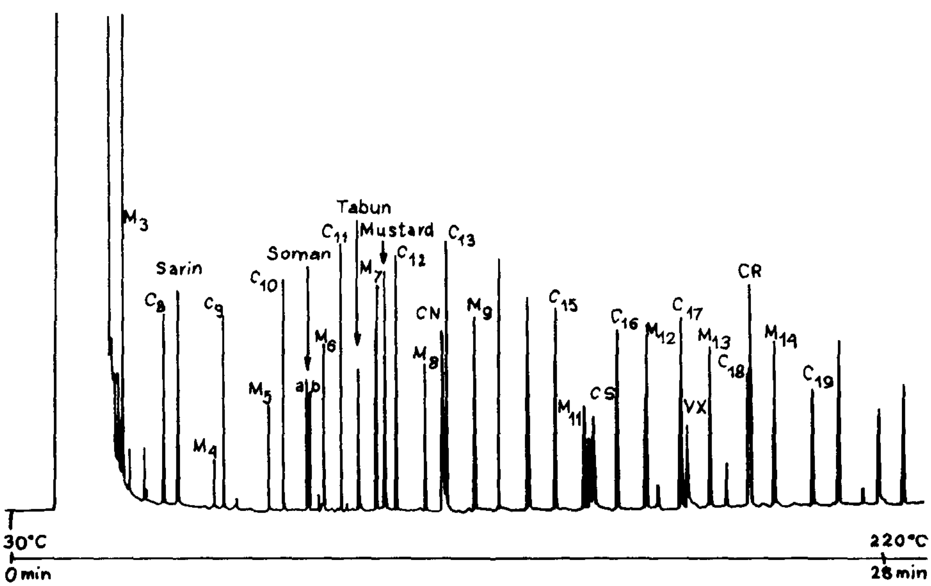


Fig. 5. Separation of chemical warfare agents and the C and M standard series mixture by GC with temperature programming. Conditions: 30 m × 0.33 mm I.D. fused-silica capillary column with 0.25-μm film of DB-5; carrier gas, helium at a flow-rate of 2 ml/min; detection, FID[13].

least two colums filled with stationary phases of different polarity. The retention indices relative to the *n*-alkane homologous series under isothermal conditions are calculated from the Kováts[212] equation and, if temperature programming is applied, form the Van den Dool and Kratz equation[213]. Usually FID or TCD is used in such instances. They allow the detection of all chemical warfare agents being separated but their sensitivities and selectivities are relatively low.

The application of a selective detector may facilitate considerably the identification of the substances being analysed. Many different selective detectors have been used in the analysis of chemical warfare agents. They may serve for detecting trace amounts of agents that contain in their molecules elements to which these detectors are particularly sensitive. Such detection methods include, electron-capture detection (ECD) for compounds containing halogens, FPD for the detection of compounds containing sulphur and phosphorus, nitrogen–phosphorus-specific detection (NPD) for compounds containing nitrogen and phosphorus, alkali flame ionization detection (AFID) and alkali thermionic detection (ATD) for organophosphorus compounds. Photoionization detection (PID) for compounds containing sulphur is gaining in importance[214,215]. Specific detectors, designed for detecting certain compounds, *e.g.*, hydrogen cyanide[216], lewisite and mustard gas[217,218], deserve mention.

Sometimes two detection methods are combined, *e.g.*, FID–AFID, FID–ECD, FID–FPD, ECD–AFID. Such systems facilitate the identification of compounds separated in one or two identical chromatographic columns[9,54,64].

Chromatographed chemical warfare agents can also be identified by confirming the presence of the compounds being detected with the use of other instrumental methods, *e.g.*, IR, NMR or MS[8,219–227]. The preferred method is combine the gas chromatograph with a mass spectrometer. Such devices are very useful for the rapid analysis of trace amounts of toxic compounds present in complex samples[220–227]. The mass spectra recorded for the components of the sample are compared with those contained in a computer memory and on this basis the particular substances are rapidly and reliably identified. The sensitivities of these devices are very good; it is possible to detect organophosphorus agents at the level of 10^{-12}–10^{-13} g[228].

The chromatographed chemical warfare agents may be identified by a technique known as retention spectrometry[13,229]. The retention spectrometer consists of several capillary columns of equal dimensions filled with stationary phases of varying polarity. After injection, the sample is divided into equal parts, each of which is directed to a different column. The same substance, after having passed through the different columns, reaches the detector, common for all columns, at different times. The registered peaks give a characteristic retention spectrum which constitutes a basis for identification of the compound of interest. This described parallel-column arrangement of retention spectrometry is used for analysing less complex samples. Samples of greater complexity are analysed by the in-series modification of retention spectrometry, in which case the sample is preliminarily separated in a conventional chromatographic column and only then is the isolated component to be determined passed to the retention spectrometer. The set-up includes two types of detection (*e.g.*, FID–TID or ECD–TID), one at the outlet of the conventional chromatographic column and the other at the outlet of the retention spectrometer. A diagram of the in-series arrangement of the retention spectrometer is shown in Fig. 6.

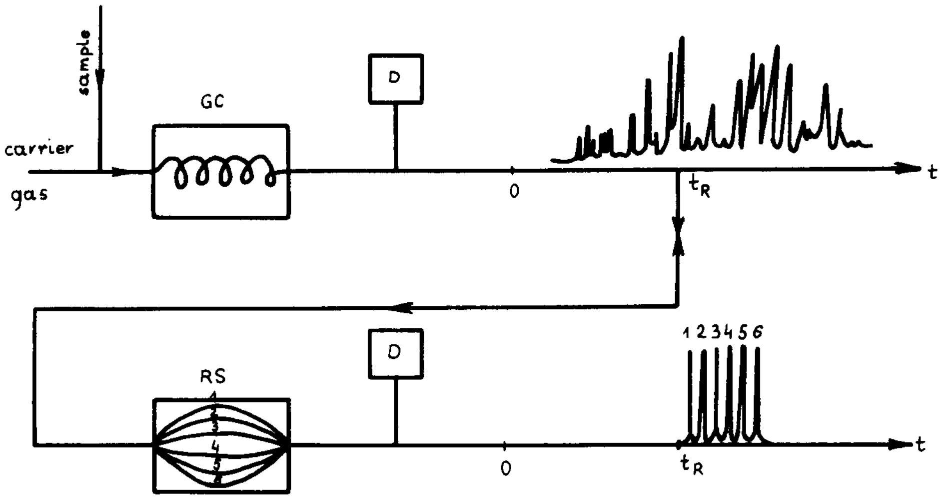


Fig. 6. Trace analysis of chemical warfare agents in complex environmental samples by in-series retention spectrometry[13].

Organophosphorus, vesicant and irritant chemical warfare agents were analysed by using a retention spectrometer including six capillary columns filled with SE-30, SE-52, SE-54, OV-1701, Carbowax 20M and OV-351[13,229].

5.2. *Organophosphorus compounds*

The earliest report on the analysis of organophosphorus chemical warfare agents appeared in 1963[230], on the analysis of sarin and its contaminants. In the course of chromatography, ghost peaks were observed whose presence was ascribed to the formation of products of sarin conversion. TCD used initially in the analysis of sarin allowed the determination of the latter at the ppm level, which was unsatisfactory in view of its high toxicity. It was only after Brody and Chaney[231] in 1966 developed a flame photometric detection system specific for phosphorus- or sulphur-containing compounds (FPD-PS) that analysis at the subnanogram level became possible[231].

Of the numerous phases on which sarin was chromatographed initially, only Apiezon M and DC-LSX-3-0295 were considered to be useful. Further studies, in which account was taken of the column life, its separating efficiency and the possibility of applying temperature programming, have shown that QF-1, Carbowax 20M and EGSS-X polyester phase give good results[43,232].

The determination of sarin in water was carried out by extraction with chloroform, adsorption on Porapak Q, thermal desorption, and column chromatography[73]. This procedure and the application of FPD made it possible to determine the content of sarin in 1 ml of water at the picogram level. Tabun, soman and VX were also determined in water[77] and the suitability of FID and FPD was compared.

Sarin, soman, DFP, tabun and VX were determined in water by the headspace method[233]. Qualitative and quantitative analysis was carried out at the ppb level. However, difficulties were encountered when analysing tabun and VX.

The direct analysis of organophosphorus agents by GC doet nos usually present any major problems[234]. However, the verification of the presence of these compounds in the contaminated environment after a prolonged residence time may present difficulties. The physico-chemical effects that lead to the lowering of concentration and/or degradation of chemical warfare agents may affect significantly the results of analysis. In water samples, products of hydrolysis of organophosphorus compounds may be present. Griest and Martin[235] made a detailed study of their analysis[235]. Direct analysis of these substances is, in view of their polarity, very difficult. Therefore, they suggested that the hydroxy group be replaced with fluorine, which was achieved by treating the organophosphorus hydrolysis products successively with dicyclohexylcarbodiimide and hydrogen fluoride. A similar method was used in the analysis of phosphono- and phosphorothiolates after their reaction with silverfluoride[236].

Organophosphorus agents undergo transformations on prolonged storage. Analysis of tabun from chemical ammunition has shown that it contains five contaminants, and VX kept for 10–15 years in glass vessels was found to contain 23 impurities, including several that were not mentioned in earlier work[47,237].

As already mentioned, FPD is very useful for organophosphorus agents and ensures good detectability. It has been found that this detectability depends considerably on the molecular structure of the chemical warfare agents[238]. This relates either to different compounds or to one compound where the separation of its isomers is involved. The importance of the latter problem is connected with the fact that some isomers are much more deadly than others and their reactions with the live organism differ.

The simultaneous separation of isomers of sarin, soman and tabun was carried out by Degenhardt and co-workers[239,240]. They separated four stereoisomers of soman and enantiomers of sarin and tabun in a short capillary column filled with a mixed stationary phase containing a chiral component. Diastereoisomers of organophosphorus compounds may also be separated in conventional analytical columns with phases such as Triton X-305 or DC-550[241]. In this connection it has been shown for seventeen selected compounds that steric and electronic effects of the P–O–C and P–F bonds play a crucial role in the separation of organophosphorus esters.

In order to establish the interactions of the particular isomers of organophosphorus warfare agents with live organisms, it is important that these isomers be determined in biological samples[242,243]. It has been found that during the detoxication of soman in rat liver its rapid racemization takes place[244].

Several studies have dealt with the determination of soman and its isomers in blood[111–113,245–247]. For this purpose capillary columns with different stationary phases, including immobilized[111,112] and optically active types[113,246,247], were used. Separation into two[111,245] and four[113,246,247] isomers was achieved. The GC separation of four stereoisomers of soman is shown in Fig. 7.

In addition to soman, the content of sarin was determined in blood of dogs when studying the mechanism of blocking acetylcholinesterase and blood proteins by these warfare agents[111], DFP has also been determined in animal tissue[248]. Machata[249] described several chromatographic systems used for the analysis of this compound in the synthesis process.

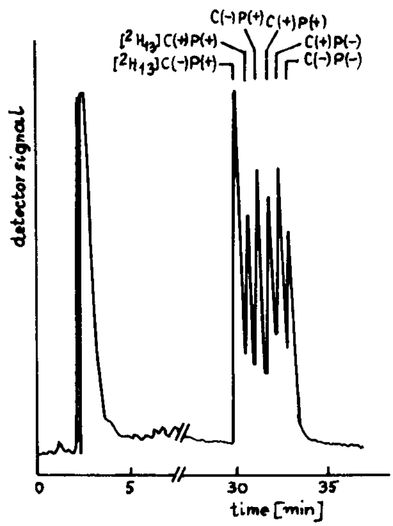


Fig. 7. Gas chromatogram of four stereoisomers [C(+)P(+)] of soman (50 pg) with internal standard C(+)P(+)[$^2H_{13}$]soman. Conditions: 50 m × 0.50 mm I.D. wide-bore capillary column; carrier gas, helium at a flow-rate of 2 ml/min; injection volume, 0.3 μl (direct injection); solvent, ethyl acetate; detection, AFID[113].

5.3. *Vesicant compounds*

Chromatographic methods were first used to analyse mustard gas in the mid-1960s. The application of FID and ECD methods made it possible to obtain satisfactory detectability of this chemical warfare agent. Today FPD with a 394-nm filter, specific for sulphur, is of particular importance as it allows the detection of mustard gas; other detection methods [coulometric Coulson detection (CCD) and Hall conductivity detection (HCD)] have also been applied to mustard gas[200].

Mustard gas often contains technological contaminants and decomposition products, *e.g.*, of hydrolysis[46,250]. The analysis has been described[250] of samples taken from chemical ammunition, soil and water which were collected from areas where the Iranian – Iraqi conflict took place. Most of the detected compounds were identified, some for the first time, and the relationship between their chemical structures and the retention parameters, were described.

A knowledge of the degradation mechanisms of vesicants makes it possible to determine the source and time of pollution by determining particular degradation products in the sample. By using GC – MS, the pollutants and products of decomposition of 2-chloroethylethyl sulphide, a product simulating mustard gas, were determined[251]. Samples stored for different periods were analysed in a capillary column. No products of oxidation or hydrolysis of the sulphide were detected. The main degradation product was 1,4-dithiane and a similar degradation mechanism to mustard gas was suggested.

The analysis of mustard gas and of the usually accompanying contaminants is conducted either in conventional analytical columns of length 0.6 – 3.0 m[40,41,46,200] or, for more complex samples (*e.g.*, biological), in capillary columns of length up to

15 m[109,250–253]. Stationary phases recommended for the analysis of mustard gas are SE-30[40], FFAP[41], QF-1[200] and SE-54[250].

In the analysis of mustard gas, tailing of peaks sometimes occurs owing to, among other things, the type of column material. The use of a PTFE column made it possible to avoid this undesirable effect[52].

Mustard gas in air is analysed after absorbing it in a non-volatile solvent[41,42]. Best solvent was diethyl succinate[42], which has more suitable properties for this purpose than hydrocarbon solvents[41].

GC may be used to assess the efficiency of protective clothing against mustard gas[40,254,255], as follows. The air containing mustard gas is passed first through the cloth from which the protective clothing is made and next through a washer with tetradecane[40]. The amount of mustard gas determined in the tetradecane allows reflects the protective efficiency of the clothing when account is taken of the concentration of mustard gas in air and the time of passage of the polluted air through the cloth.

Prior to 1982, no information was available on the use of GC for the detection of vesicants in biological materials. It was only after mustard gas was used in the Iranian – Iraqi conflict that various instrumental analytical methods, including GC, began to be used for the detection and identification of this agent in injured live organisms.

The identification of mustard gas in tissue and biological fluids (blood, serum, urine) immediately after intoxication is fairly easy[109,114,115,252,253]. Machata and Vycudilik determined mustard gas in urine of injured Iranian soldiers[109,252,253] using GC–MS with a quartz capillary column containing SE-54. The content of mustard gas determined in urine was 1–30 ppb. Heyndrickx *et al.*[114] determined mustard gas in biological samples and in soil at the picogram level using a capillary column with a non-polar phase and ECD.

It is much more difficult and sometimes even impossible to determine mustard gas in biological fluids after a certain time had elapsed after intoxication, because it undergoes complex metabolic processes. In this situation it is recommended that thiodiglycol, the main product of the hydrolysis of mustard gas is determined[118,119,253]. The analysis consists in converting this product by reaction with concentrated hydrochloric acid back to mustard gas, which is then isolated from the investigated biological material by the headspace method and subjected to GC–MS. This procedure has found, limited application, however, as it has been shown that with low thiodiglycol (55 ng/ml), it cannot be ascertained whether the mustard gas was produced from thiodiglycol or from some other substance of natural origin[118]. Recently a sensitive method for the determination of thiodiglycol in biological fluids after its conversion to bispentafluorobenzoate was reported[256]. By applying capillary GC–MS it was possible to detect thiodiglycol in amounts below 1 ng/ml in blood or urine samples.

Like mustard gas, lewisite may also be determined indirectly. Rózycki *et al.*[257] developed a method for determining lewisite in water consisting in the chromatographic determination of acetylene evolved in the reaction of *trans*-lewisite A with sodium hydroxide. In this way it was possible to determine lewisite in water at a 10^{-8}% concentration.

5.4. Irritants

Irritants are used in form of vapour or aerosols dispersed in air. The most important are tear gases such as chloroacetophenone, *o*-chlorobenzylidenemalonodinitrile, chloropicrin, dibenzo[*b*,*f*]-1,4-oxazepine, camite and sternite – adamsite.

Because of the presence of halogens in the molecules of tear gases ECD is most commonly used for their detection[11,105,201,202,258]. This method allows the analysis of tear gases at the nanogram level, whereas the more convenient FID allows their analysis only at the microgram level[11,81,201,258,259]. Also detection methods, *e.g.*, NPD, TCD and argon-ionization ones, may also be used[201,258,260].

Martz *et al.*[225] compared mass spectrometric methods combined with GC. They used mass spectrometry with electron-impact ionization (EI), positive ion chemical ionization (PICI) and with negative ion chemical ionization (NICI). For CS gas analysis, NICI affords the best results.

GC–MS systems allows the rapid analysis of irritants with good sensitivity and reliable identification[63,105,261–264]. Wils and Hulst[63] determined CN, CS and CR by GC–MS at concentrations lowers than 1 ng/ml. To achieve such a high detectability they applied a special technique of injection into the capillary column of large samples (up to 250 μl). The analyte compounds dissolved in *n*-hexane or ethyl acetate were adsorbed in a column filled with Tenax GC. After thermal desorption, the compounds were trapped in a cold fused-silica capillary column (0.3 m x 0.5 mm I.D.) coated with CP-Sil 5 CB. Next the capillary was rapidly heated and the analyte compounds were desorbed and separated in a capillary column. The peaks obtained in the mass spectrum were identified. The presence of oxygen in the injector system resulted in the appearance of a peak of oxidized CS.

Sass *et al.*[201] determined CN, CS and CA and several of their characteristic contaminants, chiefly hydrolysis products. In order to prevent the decomposition of CA catalysed by the hot metal surface, some parts of the chromatograph were made of glass.

Jane and Wheals[202] developed a method for determining CN and CS in sprayers of tear gases. They tested many chromatographic columns for this purpose and it was found that a short analytical column made of stainless steel with Carbowax 20M as the stationary phase gave good results. The use ECD made it possible to determine CS and CN at the sub-nanogram level. The use of FID was difficult as the peaks of the lachrymators coincided with those of the solvents used in atomisers. Good results were obtained when combined detection methods, *e.g.*, FID–PND or FID–ECD, were used for the detection of CS[258].

Leadbeater *et al.*[105] analysed a CS metabolite in the blood of intoxicated cats and rats. They isolated the compound from the blood sample by its extraction with *n*-hexane or ethyl acetate.

Many studies have concentrated on the GC analysis of chloropicrin, as it is used as a component of plant protection agents (fumigants) and as a monitoring substance for testing the technical soundness of filtration equipment. In the analysis of chloropicrin, ECD[32,75,100,265–271] or MS[30,74,272,273] is recommended. Other types of detection such as HCD[270,271], CCD[274], TCD[275] or FID[276] have been used less frequently. Using GC, chloropicrin has been determined in water[30,32,74,75,268,269,273,277], grain and cereals[100,270,271,275,277,278], wine[265–267], food[75] and methyl bromide[279].

The determination of chloropicrin in water is conducted by two procedures.

The first consist in isolating chloropicrin together with other volatile halogenated organic contaminants by the headspace method and then subjecting them to GC–MS. The second procedure consists in extraction of the pollutants from water with an organic solvent (usually *n*-heptane), followed by chromatography with ECD.

For the determination of chloropicrin in water, either conventional analytical columns with squalane or silicones (DC-220, DS-550 or F-50) as stationary phases or capillary columns coated with phases such as DB-5, Durabond 1, OV-1 or SE-30 were used. These methods allow the determination of chloropicrin at the nanogram level in 1 dm^3 of water.

Daft[100,270,271,278], Berck[275,280] and Kanazawa[281] determined chloropicrin residues after the application of plant protection agents in cereals and fruit. For the chromatographic separation, various columns filled with single and mixed stationary phases were used, *e.g.*, OV-17, OV-101, SE-30, SP-1000, polyethylene glycol 6000 and OV-225–OV-17 (2:1). The main problem encountered in the analysis of fumigants was to find a solvent in which the analysed compounds would be stable and which would not be eluted in the same time as the compounds being analysed; isooctane proved to be the best[100]. When ECD or HCD was used, chloropicrin could be detected at the ppb level.

Chloropicrin in wine was determined after extraction with a non-polar solvent[265–267]. Quantitative determinations at the 10 $\mu g/dm^3$ level with the use of ECD were carried out by using trichloroethylene as the internal standard.

Sometimes it may be advantageous to determine chloropicrin indirectly after its conversion to ethylene chlorohydrin by reaction with ethylene oxide[285].

Analysis of adamsite by GC is difficult and the results are often irreproducible[259] and some workers claim that at present no effective and reliable method exists. The presence in the sample of diphenylamine (substrate for the synthesis of adamsite) makes the identification of the adamsite peak almost impossible. Despite this, some possibilities of analysing adamsite do exist. In the Helsinki report[10] the analysis of adamsite decomposition products on a capillary column coated with SE-52 or OV-1 was described. FID, ECD and ATD were mentioned as being useful, and with their use it was possible to detect adamsite at the 10^{-12} g level. The problems involved in the chromatographic analysis of organoarsenic compounds have been described in several papers[53,286–289].

5.5. *Fluoroacetic acid*

Fluoroacetic acid is a representative of toxic fluoroorganic compounds classified as potential chemical warfare agents. Its sodium salt is known as compound 1080. The high toxicity of this compound requires sensitive methods of analysis. The analysis of fluoroacetic acid by conventional chemical methods is not easy in view of the difficulties in splitting the strongly polarized bond between the fluorine and carbon atoms. GC is now the most common method[48,76,103,104,106,108,235,282–284,290–299]. For detection ECD[48,76,103,108,296], FID[104,282,292,293,298] and MS[106,284,295,297] have been used; the ion-selective fluoride electrode method[48,106,295], TCD[48,291,292] and PID[298] have been applied less frequently.

The first work on the analysis of fluoroacetic acid was published by Gershon and Renwick[292]. They separated lower 2-fluoroaliphatic acids on a short copper column. It was observed that fluoroacetic acid has a longer retention time than fluoropropionic acid, which was the opposite of what would be expected from their structures and boiling points. This phenomenon was subsequently interpreted[293].

Stevens *et al.*[105] analysed fluoroacetic acid in a biological sample on a glass column filled with Porapak Q using FID. The determination of fluoroacetic acid was hindered as its peak coincides with those of other acids. They also attempted to apply GC–MS, but the results were unsatisfactory as considerable loses of the acid occurred owing to chemical reactions and/or adsorption on the metal surface of the metal tube connecting the GC column with the MS unit.

The conversion of fluoroacetic acid or its sodium salt into alkyl esters favours chromatographic analysis[48,104,106,282,290,293,295]. The production of fluoroacetic acid derivatives by reaction with *p*-bromophenacyl bromide[299], pentafluorobenzyl bromide[103,297], α-bromo-2,3,4,5,6-pentafluorotoluene[108] or N,N′-dicyclohexylcarbodiimide and 2,4-dichloroaniline[76] also proved advantageous.

Yu and Miller[104] analysed fluoroorganic acids in vegetable and animal tissues. It is assumed that the biosynthesis of toxic fluoroorganic acids due to addition of hydrogen fluoride to fragments of vegetable tissue is common for many tissues[96].

Sodium fluoroacetate is also of interest and has been determined in animal tissue[48,103,108,282,290,295–298], vegetable tissue[103,283,291], fungicides[249,290,298] and food[48]. The determination of compound 1080 in various materials was usually preceded by Soxhlet extraction with ethers, ketones or alcohols.

Casper *et al.*[297] achieved a high detectability (10 ppb) of sodium fluoroacetate by capillary GC–MS with a selective ion analyser.

Ozawa and Tsukioka[76] described a sensitive method for determining trace amounts of sodium fluoroacetate in water involving the use of ECD. This method consists in converting sodium fluoroacetate into the respective dichloroanilide derivative and chromatographic analysis of this derivative on a conventional glass column. The derivatives of other fatty acids did not interfere.

5.6. Hydrogen cyanide and cyanogen chloride

Hydrogen cyanide and cyanogen chloride are very volatile and their determination in air is difficult in view of the rapid changes in their concentration. Therefore, to ascertain that they have been used and estimate their concentration in air, advantage is sometimes taken of the fact that in an aqueous medium these compounds yield cyanide ions, which are easy to detect[11,300].

The accuracy of the chromatographic analysis of hydrogen cyanide depends strongly on the way in which the sample was collected. The aspiration method involving the use of glass or metal containers is rejected because of adsorption of hydrogen cyanide on the walls of the containers. Instead, advantage is taken of the ready adsorption of hydrogen cyanide on porous materials, from which it can be extracted with, *e.g.*, *n*-hexane or desorbed thermally[33,60,92,301]. An interesting method of collecting samples was suggested by Kuessner[44], who presented two versions for collecting trace amounts of polar substances, and also hydrogen cyanide, at dry-ice temperature (−78°C). If the matrix of the sample was still gaseous at that temperature, the gas was passed through large washers filled with a suitable solvent. If, however, the matrix condensed at −78°C, then after absorption of the sample in a polar solvent the resulting solution was warmed slowly. In this way the matrix was isolated without any losses of the compounds to be analysed. The solutions of hydrogen cyanide (and other polar compounds) obtained by one of the above methods were analysed chromatographically.

Very good detectability of hydrogen cyanide has been reported[302,303]. In one method[302] hydrogen cyanide was detected at the level of 1 pg by thermionic nitrogen detection (TND) and in the other[303] 5 pg of hydrogen cyanide were detected with AFID.

Apart from conventional chromatographic detectors, for the analysis of hydrogen cyanide the procedure suggested by Cumming and Frost[304] can be applied. It is a general procedure for nitrogen-containing compounds, in which the components of the mixture, after leaving the chromatographic column, pass through a glass column filled with copper oxide or some other compound on which, at 700°C, these compounds are oxidized to nitrogen oxides which are subsequently detected by a chemiluminescence detector.

Hydrogen cyanide has been analysed not only in air but also in other media. Woolmington[57] determined hydrogen cyanide in a mixture of permanent gases and water vapour. The height of the hydrogen cyanide peak for a mixture containing water was slightly lower (by about 1%) than that for a sample free from water. This was explained by the selective adsorption of water by the strongly active sites of the support. Such an explanation seems highly probable in view of Berezkin's study of the gas–liquid–solid system[305]. The latter also provides an explanation of why long tailing of the hydrogen cyanide peak, characteristic of polar compounds occurring at low concentrations, was sometimes observed[306]. The addition of formic acid to the stream of carrier gas improves the detectability of hydrogen cyanide six-fold[307], owing to the decrease in the total adsorption activity of the support and the decrease in the association of hydrogen cyanide molecules.

In the analysis of hydrogen cyanide in mixtures of inorganic gases, medium-polarity liquid stationary phases, *e.g.*, glyceryl triacetate, dinonyl phthalate, poly (trifluorochloroethylene), and adsorbents such as Chromosorb 104 and Polisorb-1 are used in addition to polar liquid stationary phases and Porapaks[53,58,308–316]. The analysis is usually conducted on packed columns but sometimes capillary columns coated with the SE-52 or SE-54 phases are also used[11].

Hydrogen cyanide has frequently been analysed in combustion gases[302,306,317–320] and has been detected in the products of combustion of plastics[307,321–324] and wool[325].

As already mentioned, in aqueous solution hydrogen cyanide may yield cyanides. When such a solution is treated with acids stronger than hydrogen cyanide, the latter evolves from the solution and may easily be analysed on various chromatographic columns.

Another method of analysing hydrogen cyanide in water consists in isolating it by means of an inert gas. The latter, containing the hydrogen cyanide, is then passed through a bubbler in which hydrogen cyanide is absorbed in a suitable solvent[33,60,301,326]. This method gives good results if the concentration of hydrogen cyanide is above 5 ppb.

The analysis of hydrogen cyanide in biological samples has been described[116,327,328]. Hydrogen cyanide was isolated from blood by the headspace method and the gases evolved from blood heated to 60°C were passed through a PTFE column filled with Porapak QS[116].

GC has been used to determine hydrogen cyanide in plants, fruit and products of their processing[276,280,329–331]. With chlorinating agents, *e.g.*, chloramine T, hydrogen cyanide yields cyanogen chloride which, after dissolution in ethyl acetate, toluene or hexane, can easily be determined by GC[301,332,333].

A sensitive method of determining cyanides, consisting in conversion of cyanide ions into cyanogen chloride by reaction with chloramine T, has been applied to biological samples[40,334]. In the analysis of blood, urine and stomach contents, cyanogen chloride could be detected at the 30-pg level by using ECD. Special care was taken to minimize the losses of the volatile cyanogen chloride. The procedure requires relatively large samples and is laborious.

Brunnemann *et al.*[332] identified and determined hydrogen cyanide and cyanogen in tobacco smoke by chromatography with ECD after conversion to cyanogen chloride. The amount of hydrogen cyanide in one cigarette was found to exceed 50 μg. Brown *et al.*[335] also determined cyanogen chloride in the presence of cyanogen.

5.7. *Phosgene*

Phosgene is widely applied in industry as an intermediate for the synthesis of many compounds. In the atmosphere it is generated in the lower layers of the troposphere in smog containing various chlorine compounds. In addition, phosgene is generated in the course of the thermal or photochemical decomposition of halogen solvents. Phosgene is highly toxic, so monitoring its content in air is important, especially near workers and others who may be exposed to it. Pollution of air is also possible in cases of accidents or damage to chemical works.

The chromatographic analysis of phosgene is difficult in view of its high reactivity, which corrodes the chromatograph. In addition, at low concentrations it decomposes on contact with active surfaces. For these reasons the literature on the chromatographic analysis of phosgene was sparse for some time[292,336–342]. It was only after certain components of chromatographs were made of more inert materials (PTFE, nickel, niobium, tantalum or aluminium) that the number of studies on the analysis of phosgene by GC began to increase. A gas chromatograph resistant to aggressive gaseous compounds (HCl, Cl_2, $COCl_2$, NO_2), even in the presence of water, was described by Kuessner[343]. In this instrument all the surfaces that come into contact with the sample were made of glass or PTFE.

It has been shown[344–346] that the accuracy of phosgene analysis is affected by factors such as the flow-rate of the carrier gas and the size of the injected sample. Lillian and Singh[346] showed that samples of mass up to 0.1 ng did not affect the ionization efficiency of the electron-capture detector with respect to mass. In order to lower the detection limit they used a double system of electron-capture detectors in series and were able to detect phosgene at the femtogram (10^{-15} g) level. Priestley *et al.*[339] found that the application of ECD allows phosgene to be determined at the 1–2 ppb level. The sensitivity of detection with respect to phosgene was comparable to that with respect to carbon tetrachloride (one of the best electron acceptors). In the analysis of phosgene other detectors have also been used, *e.g.*, the flame ionization detector, which allowed the detection of 0.3 μg of phosgene in 1 dm^3 of air[54], the coulometric flow-through detector[347,348], the modified Hall detector[349], mass spectrometers[30] and the detector in which use is made of a plasma discharge in argon with electrodeless excitation[350].

Phosgene has been determined in air alone[339,347,348,351–353] and in the presence of alkyl chloroformates[54], in various gas mixtures containing, *e.g.*, Ar and CO_2[336,354] or Ar, N_2, CO, CO_2, HCl and Cl_2[59,336,337,355], and also in the presence of volatile in organic chlorides[338,342,356]. Dahlberg and Kihlman[18] determined phosgene and acetyl chlorides generated in the decompostion of chloroorganic solvents and Reichert *et al.*[349] determined dichloroacetylene and its decomposition product phosgene. Many studies have been devoted to the analysis of inorganic and organic contaminants, including phosgene, in antimony, lead, titanium, tin, silicon and boron chlorides[292,338,341,357–361]. The relative retention times of phosgene and of some other chloroorganic compounds were given by Kiraly and Peter[362].

In the analysis of phosgene, chiefly liquid stationary phases were used in packed column. Capillary columns and adsorption chromatography were applied only in a few instances. Phosgene was analysed in the presence of argon and carbon dioxide, for instance, on a short silica gel column with temperature programming[354]. For more complex mixtures, systems of columns filled with liquid and solid stationary phases were used[59]. Some workers have recommended that, in view of the easy hydrolysis of phosgene, an initial adsorption column should be used to remove moisture[351–353].

Among liquid stationary phases, didecyl phthalate has been recommended for phosgene analysis[247,348]. For mixtures containing phosgene the selection of the stationary phases depends on the composition of the mixture. If acetyl chlorides were present in addition to phosgene, then the former were esterified and the resulting mixture was separated using silicone oil DC-200 or tridecyl phthalate as the stationary phase[18]. If alkylformates were present, they were converted into urea and carbamates, a normal column packed with neopentyl glycol succinate on Supelcoport or a capillary column coated with the DB-5 phase being used for their separation[54].

Phosgene is used for the derivatization of other compounds that are subsequently analysed by gas or liquid chromatography[197,363,364]. Gyllenhaal[365] applied derivatization for the indirect determinaton of phosgene and using a nitrogen detector he was able to determine 1 ng/ml levels.

Some examples of analysis of chemical warfare agents by GC are given in Table 4.

6. FINAL REMARKS

This review illustrates that chromatography is one of the most important, if not *the* most important, methods of analysis of chemical warfare agents. This conclusion reflects the well known fact that chromatographic methods are now most popular in organic analysis[366]. Chromatographic methods make it possible to analyse chemical warfare agents in complex mixtures, the detectability and sensitivity of determination being very good and the analysis times short. Various types of instruments may be used in automatic air control systems[314,367–369]. A simple instrument that combines a gas chromatograph with a mass spectrometer can be used even in field conditions[70]. This instrument may be utilized for the continuous analysis of chemical warfare agents in air and for their detection in water. Portable[370–373] and even pocket[374] chromatographs are also known.

The prospects for further progress in the analysis of chemical warfare agents by

TABLE 4

EXAMPLES OF ANALYSIS OF CHEMICAL WARFARE AGENTS BY GC

Chemical warfare agent	*Column characteristics*	*Detection*	*Detection limit*	*Conditions of analysis and remarks*	*Ref.*
Organophosphorus compounds					
Nerve gases	4.6 m x 0.32 mm I.D. fused-silica capillary columns; 0.15-μm OV-1, SE-52, SE-54, OV-1701; 0.20-μm Carbowax 20M, OV-351	FID ATD ECD	pg	30°C, 15°C/min to 200°C analysis of mixtures of agents based on 'retention spectrometry'	13 229
GB	1.83 m x 2 mm I.D. Pyrex glass column; 3% EGSS-X on Gas-Chrom Q (100–120 mesh)	FPD	0.3 ng	Nitrogen carrier gas; flow-rate, 20 ml/min; 89°C (2 min); 8°C/min to 200°C; determination in decontamination media	43 232
GA	15 m x 0.32 mm I.D. capillary columns; 0.25-μm DB-1, DB-5, DB-1701	FID MS		Helium carrier gas; linear flow-rate, 35 cm/s; 50°C (2 min), 10°C/min to 300°C; identification of 5 contaminants in munitions	47
GB	1.83 m x 3 mm O.D. PTFE column; 5% QF-1–3% DC-220 on Gas-Chrom Q (60–80 mesh)	FPD	67 pg/ml	Nitrogen carrier gas; flow-rate, 20 ml/min; 105°C; analysis in water	73
GA GB GD VX	1.83 m x 2 mm I.D. glass columns; 5% Carbowax 20M (GA) and 3% SP-2250 DB (VX); 1.83 m x 4 mm I.D. glass column; 10% SP-1000 (GB,GD)	FID FPD	0.1–0.5 ng 2–5 pg	Helium carrier gas; flow-rate, 15–30 ml/min; 130°C (GA), 170°C (GD,VX) and 150°C (3.5 min), 10°C/min to 160°C (GB); determination in water	77
GA GB GD VX	15 m x 0.32 mm I.D. fused-silica capillary columns; 0.25-μm DB-1, DB-5, DB-1701, DB-WAX	FID		Helium carrier gas; linear flow-rate, 35 cm/s; 50°C (2 min), 10°C/min to 250°C (300°C) (5 min); determination of retention indices of 22 warfare agents and simulants	91
GB GD	15 m capillary column; SE-54-HP	MS		60°C (GB), 75°C (GD) and 60°C (4 min), 25°C/min to 250°C (GB,GD); analysis in dog blood	111

GD	25 m x 0.22 mm I.D. fused-silica capillary column; CP Wax 57	NPD	40 pg/ml	Nitrogen carrier gas; flow-rate, 2 ml/min; 80°C (13 min); 40°C/min to 190°C (8 min); analysis in serum	112
GD	50 m x 0.50 mm I.D. fused-silica capillary column; Chirasil Val (Type II); 48 m x 0.50 mm I.D. fused-silica capillary column; Chirasil Val (Type I); 14 m x 0.50 mm I.D. fused-silica capillary column; Carbowax 20M	AFID	250 pg/ml	Helium carrier gas; flow-rate, 2 ml/min; 80°C; analysis of the four stereoisomers in rat blood	113
Nerve gases	3 m x 3 mm I.D. borosilicate glass column; 10% FFAP on Chromosorb W HP (80–100 mesh)	AFID ECD	1 ppb	Argon–methane carrier gas; flow-rate, 30 ml/min; 120°C; analysis in water and soil	233
Nerve gases	1.83 m x 3 mm O.D. stainless-steel column; 10% OV-61 on Chromosorb W (80–100 mesh)	FID AFID		Helium carrier gas; flow-rate, 25 ml/min; 183°C; analysis of organophosphorus compounds with hydroxyl groups in molecules	235
VX	15 m x 0.32 mm I.D. fused-silica capillary columns; 0.25-μm DB-1, DB-5, DB-1701	FID MS		Helium carrier gas; linear flow-rate, 35 cm/s; 50°C (2 min), 10°C/min to 280°C (10 min); detection of 23 contaminants in VX	237
GA GB GD VX	1.83 m x 2 mm I.D. Pyrex glass columns; 10% QF-1 on Gas-Chrom Q (80–100 mesh); SE-30 on Gas-Chrom P (80–100 mesh)	FID FPD NPD		Nitrogen carrier gas; flow-rate, 75 ml/min; or helium carrier gas; flow-rate, 40 ml/min (NPD); 60°C, 8°C/min to 200°C	238
GA GB	2 m x 0.44 mm I.D. glass capillary column; bis[(1*R*)-3-(heptafluorobutyryl)camphorate]nickel(II) in OV-101	NPD MS	pg	Helium carrier gas; linear flow-rate, 50 cm/s; 120°C; separation of stereoisomers; analysis of GA in biological fluids of animals	239
GB	2.7 m x 3 mm I.D. glass column; 25% DC-550 on Chromosorb W AW (80–100 mesh); or 3 m x 4 mm I.D. glass column; 25% Triton X-305 on Chromosorb W AW (80–100 mesh)	FID		Nitrogen carrier gas; flow-rate, 20 ml/min; 110°C	241
GD	1.5 m glass column; 10% SP-1200–1% H_3PO_4 on Chromosorb W AW DMCS (80–100 mesh)	MS		95°C (1 min), 8°C/min to 130°C; analysis of stereoisomers in rat liver	244

(Continued on p. 388)

TABLE 4 (*continued*)

Chemical warfare agent	*Column characteristics*	*Detection*	*Detection limit*	*Conditions of analysis and remarks*	*Ref.*
GD	20 m x 0.32 mm I.D. glass capillary column; SP 1000 WCOT	MS	5 ng/ml 5 ng/g	Helium carrier gas; flow-rate, 2 ml/min; determination in nerve tissue and blood of mice	245
GD	25 m x 0.3 mm I.D. capillary column; Chirasil-Val; 30 m x 0.3 mm I.D. capillary column; Carbowax 20 M–Chirasil-Val	FID		80°C; separation 4 stereoisomers in rat blood, in liver homogenates of rats and on passage through excised guinea pig skin	246
GD	2 m x 0.44 mm I.D. glass capillary column; bis[(1*R*)-3-(heptafluorobutyryl)camphorate]nickel(II) in OV-101	AFID	30 pg per 3 ml	Separation of 4 stereoisomers in blood	247
DFP	15% XF-1150 on Gas-Chrom Q	FPD	<1 ng	Analysis of residues in pig tissues	248
GB	1.83 m x 3 mm O.D. PTFE column; 3% DC-200–5% QF-1 on Gas-Chrom Q (60–80 mesh)	FPD	0.1 $\mu g/dm^3$	Nitrogen carrier gas; flow-rate, 30 ml/min; 120–150°C; automated analysis of air	367
Vesicant compounds					
HD	4.6 mm x 0.32 mm I.D. fused-silica capillary columns; 0.15 μm, OV-1, SE-52, SE-54, OV-1701; 0.20-μm, Carbowax 20M, OV-351	FID ATD ECD	ng	30°C, 15°C/min to 200°C; analysis of mixtures of agents based on 'retention spectrometry'	13 229
HD	3 m x 3 mm O.D. stainless-steel column; 10% SE-30 on Diatoport S (60–80 mesh)	FID	5 ng	Helium carrier gas; flow-rate, 60 ml/min; 125°C	40
HD	0.61 m x 3 mm I.D. stainless steel column; 2% FFAP on Chromosorb W AW DMCS (60–80 mesh)	ECD	0.2 ng	Argon–methane (95:5) carrier gas; flow-rate, 23 ml/min; 150°C; air analysis	41
HD	1.83 m x 3 mm O.D. stainless-steel column; 4% FFAP on Chromosorb W AW DMCS (60–80 mesh)	FPD	0.2 ng	Nitrogen carrier gas; flow-rate, 55 ml/min; 155°C; air analysis	42

HD	1.5 m x 2 mm I.D. glass column, 3% cyclohexanedimethanol succinate on Gas-Chrom Q (100–120 mesh)	FID	μg	Helium carrier gas; flow-rate 35–40 ml/min; 120°C or 110°C, 28°C/min to 230°C; separation of HD, halfmustard and thiodiglycol	46
HD	1.83 m x 3 mm O.D. PTFE column 2% SE-30 and 5% Carbowax 4000 on Chromosorb 750 (60–80 mesh)	FPD	ng	Nitrogen carrier gas; flow-rate, 25 ml/min; 140°C; air analysis	52
HD	15 m x 0.32 mm I.D. fused-silica capillary columns; 0.25-μm DB-1, DB-5, DB-1701, DB-WAX	FID		Helium carrier gas; linear flow-rate 35 cm/s; 50°C (2 min), 10°C/min to 250°C (300°C) (5 min); analysis in soil; determination of retention indices of 22 warfare agents and simulants	91
HD	25 m x 0.32 mm I.D. fused-silica capillary column; polydiethylsiloxane (CP tm Sil S)	ECD	pg	Argon–methane (90:10) carrier gas; 55°C (5 min), 5°C/min to 120°C, 10°C/min to 300°C (10 min); analysis in biological samples and soil	114
HD HN-3	1.83 m x 6 mm O.D. Pyrex glass column; 10% QF-1 on Gas-Chrom Q (60–80 mesh) or 3% QF-1 on Gas-Chrom Q (100–120 mesh)	FID ECD FPD-S,P HCD	40 ng 0.2 ng 0.7–2 ng 5 ng	Helium carrier; flow-rate, 40 ml/min; or argon–methane (90:10) (ECD); flow-rate, 90 ml/min; 100°C or 60°C, 8°C/min to 230°C	200
HD	15 m x 0.32 mm I.D. fused-silica capillary columns; 0.25-μm DB-1, DB-5, DB-1701	FID		Helium carrier gas; linear flow-rate, 35 cm/s; 50°C (2 min), 10°C/min to 300°C (5 min); determination of retention indices for 37 sulphur vesicant and vesicant-related compounds	251
HD	15 m x 0.32 mm I.D. fused-silica capillary column; SE-54	MS	10 ng/μl	Helium carrier gas; flow-rate, 6 ml/min; 50°C, 20°C/min to 280°C; urine analysis	252
L	2.1 m x 4 mm I.D. glass column; silica gel (30–75 mesh)	FID	10^{-7} g/dm^3	Nitrogen carrier gas; flow-rate, 40 ml/min; 180°C; analysis in water	257
HD	1.83 m x 3 mm O.D. PTFE column, 3% DC-200–5% QF-1 on Gas-Chrom Q (60–80 mesh)	FPD	3 μg/dm^3	Nitrogen carrier gas; flow-rate, 30 ml/min; 120–150°C; automated analysis of air	367

(Continued on p. 340)

TABLE 4 (*continued*)

Chemical warfare agent	*Column characteristics*	*Detection*	*Detection limit*	*Conditions of analysis and remarks*	*Ref.*
Irritant compounds					
CN CR CS	4.6 m x 0.32 mm I.D. fused-silica capillary columns; 0.15 μm, OV-1, SE-52, SE-54, OV-1701; 0.20 μm, Carbowax 20M, OV-351	FID ATD ECD	ng	30°C, 15°C/min to 200°C; analysis of mixtures of agents based on 'retention spectrometry'	13 229
CN CR CS	50 m x 0.3 mm I.D. fused-silica capillary column; Chrompack (CP Sil 8 CB)	MS	< 5 ng	Nitrogen carrier gas; flow-rate, 30 ml/min; 80°C, 10°C/min to 240°C	63
CN CR CS	15 m x 0.32 mm I.D. fused-silica capillary columns; 0.25-μm DB-1, DB-5, DB-1701, DB-WAX	FID		Helium carrier gas; linear flow-rate, 35 cm/s; 50°C (2 min), 10°C/min to 250°C (300°C) (5 min); determination of retention indices of 22 warfare agents and simulants	91
CS	1.5 m x 3.1 mm I.D. Pyrex glass columns; 10% polyethylene glycol adipate or 10% Apiezon L on Celite (100–200 mesh); 0.4 m x 2.2 mm I.D. stainless-steel column; 5% phenyldiethanolamine succinate on Chromosorb G (85–100 mesh)	ECD MS		Nitrogen carrier gas; flow-rate, 60 ml/min; 185°C; and helium carrier gas (MS); flow-rate, 15 ml/min; 170°C; analysis in cat and rat blood	105
CA CN CS	1.7 m x 6 mm O.D. borosilicate glass column; 10% QF-1 on Gas-Chrom Q (60–80 mesh)	TCD FID ECD	mg μg 4 ng (CA) 0.2 ng (CN) 0.1 ng (CS)	Helium carrier gas; flow-rate, 90 ml/min; 130°C (CA,CN), 150°C (CS) and 65°C, 6°C/min to 200°C; detection and determination in gases and liquids	201
CN CS	0.9 m x 2.2 mm I.D. stainless-steel column; 2% Carbowax 20M on Chromosorb G (80–100 mesh)	ECD FID	>0.2 ng 2–5 ng	Nitrogen carrier gas; flow-rate, 30 ml/min; 60 and 180°C; analysis in tear gas aerosols	202

CS	1.5 m x 4 mm I.D. glass column; 3% SE-30 on Chromosorb G-HP (80–100 mesh) (I); or 4 m x 3 mm I.D. glass column; 3% OV-1 on Chromosorb W HP (80–100 mesh)(II)	FID–ECD FID–NPD		Nitrogen carrier gas; flow-rate, 60 ml/min (I); and helium carrier gas; flow-rate, 50 ml/min (II); *determination of retention indices for* 296 substances	258
CN CS DM	1.83 m x 3 mm I.D. Pyrex glass column; 3% OV-17 on Varaport 30 (100–120 mesh)	FID	μg	Nitrogen carrier gas; flow-rate, 25 ml/min; 55°C, 12°C/min to 210°C; analysis in mixtures; with other irritants and their impurities	259
CN CS	1.83 m x 3 mm I.D. glass column; 3% OV-1 on Gas-Chrom Q (60–80 mesh)	AID	μg	Argon carrier gas; flow-rate, 50 ml/ml; 145°C; analysis in blood and tissue	260
CN	1 m column; 5% OV-17	MS	ng	25°C (22 min), 8°C/min to 250°C	262
PS CG	25 m x 0.25 mm I.D. silica gel capillary column; SE-30–OV-1 (1:1)	MS		Helium carrier gas; 0–180°C (200°C); determination of volatile organic compounds in decontaminated water	30
PS	25 m x 0.2 mm I.D. fused-silica capillary column; 0.3-μm OV-1 (I); or 3 m x 2 mm I.D. glass column; 10% Squalane on Chromosorb W AW (80–100 mesh)(II)	ECD		Helium carrier gas; 35°C (1 min), 20°C/min to 70°C (1 min), 3°C/min to 225°C (I); or argon–methane carrier gas; flow-rate, 25 ml/min; 67°C (II); analysis in drinking water	32
PS	30 m x 0.32 mm I.D. fused-silica fused capillary column; 1.0 μm DB-5	MS		Helium carrier gas; −50°C, 30°C/min to 50°C, 5°C/min to 240°C; identification in groundwater	74
PS	60 m fused-silica capillary column; Durabond 1	ECD	10 pg	Nitrogen carrier gas; 40°C (35 min), 5°C/min to 160°C; analysis of 16 chloroorganic compounds in water, waste water and food	75
PS	1.83 m x 4 mm I.D. glass columns; 20% OV-225–20% OV-17 (2:1), 20% OV-101 *and* 20% OV-17 on Chromosorb W HP (80–100 mesh)	ECD	ppm	75–85°C; analysis of 7 fumigants in food	100
PS	10% SE-30 on Chromosorb W AW (80–100 mesh)	ECD		Analysis in wine	266

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TABLE 4 (*continued*

Chemical warfare agent	*Column characteristics*	*Detection*	*Detection limit*	*Conditions of analysis and remarks*	*Ref.*
PS	QF-1, QV-17 on Chromosorb W (80–100 mesh)	ECD	< 0.01 mg/dm^3	Analysis in wine and high alcoholic beverages	267
PS	Glass columns with squalane, silicone DC-200, silicone Versilube F-50	ECD	0.06 μg/dm^3	Analysis in drinking water with other halogenated compounds	269
PS	1.8 m x 4 mm I.D. or 3.6 m x 4 mm I.D. glass columns; 20% OV-101, 10% SP-1000, 20% OV-17 and 20% OV-225–20% OV-17 (2:1) on Chromosorb W (80–100 mesh)	ECD HCD	0.2 ng	80–90°C; determination of 10 fumigant residues in grain and grain-based products	270
PS AC	1.83 m x 6 mm O.D. stainless-steel column; 10% SE-30 on Diatoport S (60–80 mesh)	TCD		50°C, 15°C/min to 180°C; separation of 34 fumigants	275
PS	50 m x 0.2 mm I.D. fused-silica capillary column; SP-1000 WCOT	FID		Nitrogen carrier gas; linear flow-rate, 10 cm/s; 20°C (5 min), 2°C/min to 250°C; determination of retention indices for 221 chloroorganic compounds	275
			Industrial compounds		
FCH_2COOH	2 m x 4 mm I.D. glass columns; 10% polyethylene glycol 6000 (I) and 10% Reoplex 400 (II) on Chromosorb W AW DMCS (60–80 mesh)	FID		Helium carrier gas; 65°C, 3°C/min to 215°C (I) and 50°C (60°C), 43°C/min to 200°C (II); analysis in plant tissue and organs of animals	104
FCH_2COOH	1.5 m x 4 mm I.D. glass column; Porapak Q	MS FID	0.1 μg/g	Helium carrier gas; flow-rate, 30 ml/min; 200°C; determination in animal tissues	106
FCH_2COOH	0.4 m x 6 mm I.D. column; 10% Reoplex 400 on Chromosorb W (60–80 mesh)	TCD		Analysis of 10 carboxylic acids in plant samples	288

FCH_2COOH	1 m x 6 mm O.D. copper column; 15% Tween 80–H_3PO_4 (9:1) on Chromosorb W (30–60 mesh) (I); 2.2 m x 3 mm O.D. copper column; 10% Tween 80–H_3PO_4 (9:1) on firebrick (100–120 mesh)(II)	TCD FID		Helium carrier gas; flow-rate, 90 ml/min; 132°C (I); nitrogen carrier gas; flow-rate, 30 ml/min; 156°C (II); separation and identification of C_2–C_6 fluorinated fatty acids	292
FCH_2COOH	1.5 m x 3 mm O.D. stainless-steel column; 5% DEGS on Chromosorb W (80–100 mesh)	FID		Nitrogen carrier gas; flow-rate, 25 ml/min; 85 or 100°C, 5°C/min to 200°C; analysis of mixtures of methyl esters of 2-fluoro-fatty acids up to C_{18}	293
FCH_2COONa	1.83 m x 3 mm I.D. or 1.83 m x 6 mm I.D. glass columns; Resoflex; 7.6 m x 3 mm I.D. or 7.6 m x 6 mm I.D. glass column; Resoflex	TCD ECD	 0.1 μg	Nitrogen carrier gas; flow-rate, 50 ml/min; 75°C; analysis in biological tissue, food and baits	48
FCH_2COONa	2.1 m x 3 mm I.D. glass columns; Apiezon L–H_3PO_4 (5 + 2%) and DEGS–H_3PO_4 (5 + 1%) on Chromosorb W (60–80 mesh)	ECD	0.03 ng	Nitrogen carrier gas; flow-rate, 20 ml/min; 175°C; determination in water	76
FCH_2COONa	1.83 m × 2 mm I.D. Glass column; 3% DC-200 or 3% DC-200 and 5% QF-1 (1:1) on Chromosorb W (100–120 mesh)	ECD	0.2 ppm	Argon–methane (90:10) carrier gas; flow-rate, 20 or 40 ml/min; 105°C; determination in grain samples and animal tissues	103
FCH_2COONa	1.83 m x 3 mm I.D. or 1.83 m x 6 mm I.D. glass columns; Resoflex	MS	0.1 μg	Nitrogen carrier gas; flow-rate, 50 ml/min; 75°C; determination in biological samples	295
FCH_2COONa	0.9 m x 3 mm I.D. aluminium column; Chromosorb 102 (100–120 mesh)	FID	0.1–0.2 ppm	Nitrogen carrier gas; flow-rate, 30–35 ml/min; 155 or 180°C; determination in plant tissue	282
AC	1.0–5 m columns; Porapak T or Q	TCD FID	1 ppb 1 ppm	Hydrogen carrier gas; flow-rate, 50 ml/min; 120°C (130°C) or 120°C (2 min), 5°C/min to 145°C (5 min), 25°C/min to 200°C (11 min); analysis in gaseous mixture	44
AC	2.1 m x 8 mm O.D. stainless-steel column; 20% polyethylene glycol 1500 on Chromosorb or Celite (30–60 mesh); and 1.0 m x 6 mm I.D. glass column; molecular sieve 5A	TCD		Analysis in gaseous mixture	57

(*Continued on p. 344*)

TABLE 4 (*continued*)

Chemical warfare agent	*Column characteristics*	*Detection*	*Detection limit*	*Conditions of analysis and remarks*	*Ref.*
AC	2.4 m x 5 mm I.D. copper column; 25% glyceryl triacetate on Chromosorb P (30–60 mesh) (I); and 2.7 m x 5 mm I.D. copper column; molecular sieve 5A or 13X (II)	TCD		75°C (I) and 20°C (II); determination AC and cyanogen in presence of CO_2, O_2, N_2, CH_4 and CO	58
AC	5.5 m x 6 mm I.D. stainless-steel column; 20% dinonyl phthalate on Chromosorb W	TCD	25 $\mu g/dm^3$	Helium carrier gas; flow-rate, 135 ml/min; 44°C; analysis in water	60
AC	25 m x 0.22 mm I.D. fused-silica capillary column; CP-SIL 5	MS		Helium carrier gas; 0°C, 3°C/min to 275°C; analysis in soil by pyrolysis gas chromatography	92
AC	1.83 m x 3 mm O.D. PTFE column; Porapak QS	ATD	$5 \cdot 10^{-8}$ g/ml	Helium carrier gas; flow-rate, 30 ml/min; 80°C; analysis in blood	116
AC	1.83 m x 6 mm O.D. stainless-steel column; 10% SE-30 on Diatoport S (60–80 mesh)	TCD		50°C, 15°C/min to 180°C; separation of 34 fumigants	275
AC	0.9 m x 2 mm I.D. glass column; Chromosorb 101 (80–100 mesh)	TID-N	1 pg	Air analysis	302
AC	3.6 m x 3 mm O.D. stainless-steel column; 5% Carbowax 400 on Teflon 6	FID	< 10 ppm	Helium carrier gas; flow-rate, 21 ml/min; 60°C; determination in hydrocarbon combustion effluents	306
AC	2 m x 3 mm I.D. stainless-steel column; Silochrom S-80 with 4–8% H_3PO_4	FID		Argon carrier gas; flow-rate, 33 ml/min; 100°C; determination of pyrolysis products of poly-urethane foams	307
AC	6 m x 6 mm I.D. glass column; Daifuloil No. 1, 3 and 50 [poly(trifluorochloroethylene)] on Polifulon powder (30–60 mesh)	TCD		Ambient temperature; analysis of reactive inorganic gases and vapours	308

AC	3 m x 3 mm I.D. column; Polisorb 1	TCD		45°C; analysis of hydrogen sulphide gas	312
AC	2 Columns, 5–7% cyanoethylated pentaerythritol and 2–7% diglycerol on Polisorb 1	TCD		95°C; analysis of products of oxidative ammonolysis of propylene	313
AC	2.8 m x 4 mm I.D. stainless-steel column; 20% dinonyl phthalate on Dinokhrom N	TCD		54°C; determination with $(CN)_2$	315
AC	3 m Column; Porapak Q (50–100 mesh); 2.5 m column, 15% polypropylene glycol on Chromosorb AW DMCS (60–70 mesh)			35°C; analysis of exhaust gases	317
AC	3 m x 4 mm I.D. column; Porapak Q	FID	<0.1 ppm	30°C, 2°C/min to 50°C, 5°C/min to 200°C; determination in exhaust gases	318
AC	2 m x 1 mm I.D. glass column; 7% Carbowax 20M on Chromosorb W (80–100 mehs); and 4 m x 4 mm I.D. glass column, 7% triacetin on Chromosorb W (80–100 mesh) (I); 2 m x 2 mm I.D. stainless-steel column, 5% dimethylsulpholane on Inerton AW (90–120 mesh) (II)	FID TCD	$7 \cdot 10^{-10}$ g $3.5 \cdot 10^{-7}$ g	Helium carrier gas; flow-rate, 30 ml/min; 40°C (I) and 20°C (II); quantitative analysis of pyrolysis products formed during thermal degradation of polymers	324
AC	2 m x 3 mm I.D. column; Porapak Q			Determination in unsweetened bean jam	330
AC	1.83 m x 6 mm O.D. stainless-steel column; 7% Halcomid M-18 on Anakrom AB5 (90–110 mesh)	ECD	$12.5 \cdot 10^{-12}$ g	Argon–methane (95:5) carrier gas; flow-rate, 40 ml/min; 55°C; determination of cyanide in biological samples	334
CK	1.5 m x 3 mm I.D. column; Porapak QS	FID TCD	$2 \cdot 10^{-11}$ mol $4 \cdot 10^{-11}$ mol	Helium carrier gas; flow-rate, 34.5 ml/min; 90°C; comparative study of the response two detectors to CK and $(CN)_2$	335
CG	2 m x 3 mm I.D. stainless-steel column; 20% silicone oil DC-200 on Chromosorb W	ECD	< 1 ppb	Argon–methane (95:5) carrier gas; flow-rate, 30 ml/min; 25°C; analysis of mixture of acetyl chlorides in air	18
CG	25 m x 0.25 mm I.D. silica gel capillary column; SE-30 and OV-1 (1:1)	MS		Helium carrier gas; 0–180°C (200°C); determination of volatile organic compounds in decontaminated water	30

(Continued on p. 346)

TABLE 4 (*continued*)

Chemical warfare agent	*Column characteristics*	*Detection*	*Detection limit*	*Conditions of analysis and remarks*	*Ref.*
CG	3 m x 3 mm O.D. nickel column; 10% neopentyl glycol succinate on Supelcoport (100–120 mesh); or 30 m x 0.32 mm I.D. fused-silica capillary column; DB-5	FID	0.7 μg	190°C or 150°C (16 min), 16°C/min to 190°C; simultaneous determination of CG and chloroformates in air	54
CG	1 m x 6 mm I.D. stainless-steel column; 28.3% Apiezon N on Sterchamol	TCD		Hydrogen carrier gas; 100°C; analysis of impurities in $SiCl_4$, $SnCl_4$ and $TiCl_4$	338, 341
CG	2 m x 4.7 mm I.D. aluminium column; 30% Flexol 10-10 (didecyl phthalate) on GC-22 Super Suport (100–120 mesh)	ECD	2 ng	Nitrogen carrier gas; flow-rate, 50 ml/min; 50°C; automated air analysis	339
CG	3 m x 6 mm O.D. aluminium column; 30% didecyl phtalate on Chromosorb P (100–120 mesh)	2 ECD	10^{-15} g	Nitrogen carrier gas; flow-rate, 37 ml/min; 23°C; determination in air	347
CG	5.5 m x 6 mm I.D. aluminium column; 30% silicone oil DC-200 on Chromosorb P (100–120 mesh)	2 ECD	0.28 ppm	Nitrogen carrier gas; flow-rate, 60 ml/min; 23°C; analysis of 8 halogenated hydrocarbons in urban air	348
CG	1.83 m x 2 mm I.D. column; 30% Squalane on Chromosorb W AW (100–120 mesh)	ECD	ppb–ppm	Helium carrier gas; flow-rate, 30 ml/min; 80°C; detection of dichloroacetylene and its decomposition product CG	349
CG	2.5 m x 1.5 mm I.D. aluminium column; 30% diisodecyl phthalate on Aeropak (80–100 mesh)	ECD	0.02 ppm	Nitrogen carrier gas; flow-rate, 30 ml/min; 50°C; determination of CG and dichloroacetylene in air	351

CG	3 m x 3 mm I.D. PTFE column; Chromosil 310	ECD	1 ppb	Argon–methane (95:5) carrier gas; flow-rate, 15 ml/min; 30°C; air analysis	352
CG	0.15 m x 3 mm O.D. column; silica gel A-40 (30–60 mesh)	TCD		Helium carrier gas; flow-rate, 20.5 ml/min; 30°C (3 min)–150°C; analysis of CG, CO_2 and Ar mixture	354
CG	9 m x 4.2 mm I.D. PTFE column; 10% Arochlor 1232 on Chromosorb T (40–60 mesh)	Mass detector		Helium carrier gas; flow-rate, 200 ml/min; 32°C; analysis in CO, CO_2, HCl and Cl_2 mixture	355
CG	Glass column; 10–15% polymethylsiloxane PMS-20, PMS-100, PMS-200 on Spherochrome 1	TCD TID		Nitrogen carrier gas; analysis of inorganic compounds in $SiCl_4$ and $GaCl_3$	357
CG	0.4 m x 4 mm I.D. column; 15% polyethylene glycol 6000 or polymethylsiloxane PMS-100 on Hezasorb	FID TCD MS		Nitrogen carrier gas; flow-rate, 26 ml/min; 140°C; analysis of purity of $PbCl_4$ and $SbCl_4$	358
CG	4 m x 4.5 mm I.D. glass column; 16% dinonyl phthalate or 16% silicone elastomer E-301 on Chromaton N AW HMDS	FID TCD		Nitrogen carrier gas; flow-rate, 45 ml/min; 50°C; determination of impurities in $SiCl_4$	359
CG	0.6 m x 4 mm I.D. column; 20% diphenylamine on Spherochrome 1	MS		Helium carrier gas; 140°C; identification of impurities in $PbCl_4$	361
CG	1.2 m x 2 mm I.D. glass column; 3% Hi-EFF-BBP on Gas-Chrom Q (100–120 mesh); and 0.6 m x 2 mm I.D. glass column; 3% Carbowax 20M on Gas-Chrom Q (100–120 mesh)	NPD	1 ng/ml	Nitrogen carrier gas; flow-rate, 30 ml/min; 200 or 240°C; determination after cyclization with a 2-hydroxyamine	365

chromatographic methods are very good, owing to the progress in the collection and preparation of samples for chromatographic analysis[38,375–380] and the development of particular chromatographic methods[381,382]. The latter relates especially to GC[383–388] and TLC[389,390]. The recent rapid development of supercritical fluid chromatography (SFC) also deserves attention. It seems that SFC, which has not so far been applied in the analysis of chemical warfare agents, may be particularly useful for the purpose[391–395].

Since the completion of the literature survey, a number of papers relevant to the chromatographic determination of chemical warfare agents have been published[396–413]. Among the agents studied were PS[396,398,404,406], HD[397,399,401], GA[400,405], GB[400,403,405], GD[400,401,405], VX[400,403,405,412], BZ[402], PF-3[405] and sodium monofluoroacetate[410].

7. SUMMARY

The usefulness and applications of the particular types of chromatography in the analysis of chemical warfare agents have been reviewed. A major problem in the chromatographic analysis of chemical warfare agents is the collection and preparation of the samples. The importance of this problem differs for the various types of chromatography. Significant differences occur in the way in which samples are collected from air, water, soil, vegetables or animal organisms.

The analyses are characterized by the main groups of chemical warfare agents, *e.g.*, organophosphorus, vesicants, irritants, etc. Account has been taken of the relationships between their properties and the possibilities of their chromatographic analysis. The advantages and disadvantages of particular types of chromatography in the analysis of the particular groups and individual agents have been considered. The detectability of particular chemical warfare agents has been assessed, together with the separating efficiency for their mixtures. Examples of applications of chromatographic systems and conditions of chromatographing are summarized in tables.

It is concluded that chromatography is a very useful tool in the analysis of chemical warfare agents; GC and TLC have the most advantageous properties, HPLC being slightly inferior.

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