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IDENTIFICATION AND DETERMINATION OF SOME UREA, CARBAMATE AND THIOCARBAMATE DERIVATIVES IN AIR

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SUMMARY

The use of UV spectrophotometry, thin-layer chromatography (TLC) and gas-liquid chromatography (GLC) for the identification and determination of some carbamate, thiocarbamate acid and urea derivatives is described. For the separation of carbamate and thiocarbamate pesticides TLC and GLC are applied. Methods for obtaining airborne samples are described and the results of the determination of some pesticides by different methods are presented.

INTRODUCTION

The increasing use of herbicides and pesticides has led to environmental contamination problems, including air. Among the many chemical combinations used as pesticides, urea, carbamate and thiocarbamate derivatives are of great importance. This paper describes methods for the identification and determination of such compounds in air.

In accordance with requirements¹ for methods for air analysis in working zones, the duration of taking air samples should not exceed 30 min when determining pesticides at the level of half of the maximum allowable concentration (MAC). Proceeding from these requirements, the lower limit of detection of the substance in 1 m³ of air should not exceed half of the MAC.

Table I lists the MACs of carbamate, thiocarbamate and urea derivatives¹ and the maximum possible concentrations of their vapours in air calculated by us according to their saturated vapour pressures^{2,3} and also obtained experimentally are given. As shown in Table I, the MAC of pesticides in air in working zones fluctuates within the range 0.2–5 mg m⁻³ and the maximum possible concentrations of their vapours in air are 0.12–54.2 mg m⁻³ for carbamates, 0.03–0.3 mg m⁻³ for urea and 23–357 mg m⁻³ for thiocarbamates. Hence maximum possible concentrations of pesticide vapours exceeding the MAC by many times occur for some carbamate derivatives and all

TABLE I

MAC AND MAXIMUM POSSIBLE VAPOUR CONCENTRATION OF SOME PESTICIDES IN THE WORKING ZONE AIR

Systematic name	Pesticide name		MAC (mg m ⁻³)	Saturated vapour pressure (mmHg)	Max. possible concentration (mg m ⁻³)
	ISO	U.S.S.R.			
3-Methoxycarbonylamino-phenyl-N-(3-methylphenyl)carbamate	Phenmedi-pham	Beta-nal	0.5	0.14 · 10 ⁻⁴	0.2(20°C)
4-Chlorbutyne-2-yl-N-m-chlorophenylcarbamate	Barban	Carbyne	0.5	5.02 · 10 ⁻⁴	7(25°C)
Isopropyl-N-phenylcarbamate	Propham	IFC	2.0		6.4(20°C)
Isopropyl-N-(3-chlorophenylcarbamate)	Chlorpropham	Chlor-IFC	2.0	10 ⁻⁵ -10 ⁻⁶	0.1 0.01(25°C)
1-Naphthyl-N-methylcarbamate	Carbaryl	Sevin	1.0	5 · 10 ⁻³	54.2(26°C)
5,6-Dimethyl-2-dimethylamino-4-pyrimidinyl dimethylcarbamate	Pyrimicarb	Pyrimor	0.2	30 · 10 ⁻⁶	0.37(30°C)
S-Propyldipropylthiocarbamate	Vernolat	Vernam	5.0	10.9 · 10 ⁻³	119.4(25°C)
S-Ethylcyclohexylthiocarbamate	Cycloate	Roneet	1.0	2 · 10 ⁻³	23.4(25°C) 93(20°C)
S-Ethyl-N,N-diisobutylthiocarbamate	Butylate	Sutan	—	13.0 · 10 ⁻³	152(25°C)
S-Propyl-N-ethyl-N-butylthiocarbamate	Pebulate	Tillam	1.0	0.01	109.4(25°C)
S-Ethyl-N,N-di-n-propylthiocarbamate	EPTC	Eptam	2.0	35 · 10 ⁻³	357(25°C)
S-Ethyl-1-hexamethyleniminiothiocarbamate	Ordram	Yalan	0.5	0.005	56(25°C)
N-3,4-Dichlorophenyl-N,N-dimethylurea	Diuron	Diuron	5.0	0.31 · 10 ⁻⁵	0.03(50°C)
1,3-Bis-(2,2,2-trichloro-1-oxyethyl)urea		DCM	5.0		0.3(20°C)

thiocarbamate derivatives listed. This determines the method of taking air samples for pesticide analysis, depending on the state of the substance involved.

In the literature, conditions for the chromatographic separation of numerous pesticides, including phenylurea, carbamate and some thiocarbamate derivatives, from vegetables, soils and animal tissues have been described. The methods used included thin-layer chromatography (TLC) and gas-liquid chromatography (GLC) with flame-photometric, electrolytic conductivity and nitrogen (N-FID) detectors³⁻⁷. The application of high-performance liquid chromatography (HPLC) for the determination of carbamate insecticide⁸ has also been described. There is little information on methods for the determination of urea, carbamate and thiocarbamate derivatives in air⁹⁻¹¹.

We have investigated the possibility of identifying and determining some urea, carbamate and thiocarbamate derivatives in air by means of UV spectrophotometry, TLC and GLC.

EXPERIMENTAL AND RESULTS

UV spectrophotometry

UV absorption spectra of chemically pure substances were measured at room temperature ($20 \pm 3^\circ\text{C}$) using SF-4a and SF-16 spectrophotometers in quartz cuvettes ($l = 1 \text{ cm}$) with 96% ethanol and *n*-hexane as solvents.

Table II gives wavelengths of maximum absorption and molar absorptivities.

TABLE II

ϵ_{max} AND λ_{max} OF ABSORPTION OF UREA, CARBAMATE AND THIOCARBAMATE DERIVATIVES

Type	Pesticide	Empirical formula	λ_{max}	ϵ_{max} ($l \text{ mol}^{-1} \text{ cm}^{-1}$)	Solvent
Thiocarbamates	Diptal	$\text{C}_{10}\text{H}_{16}\text{ONCIS}$	249	$0.31 \cdot 10^4$	<i>n</i> -Hexane
			254–255	$0.56 \cdot 10^4$	Ethanol
	Roneet	$\text{C}_{11}\text{H}_{21}\text{ONS}$	233	$1.54 \cdot 10^3$	<i>n</i> -Hexane
			272	$0.33 \cdot 10^3$	
			232	$0.88 \cdot 10^3$	Ethanol
			272	$0.14 \cdot 10^3$	
	Eptam	$\text{C}_9\text{H}_{19}\text{ONS}$	255	$0.67 \cdot 10^3$	<i>n</i> -Hexane
			255	$0.14 \cdot 10^3$	Ethanol
	Yalan	$\text{C}_9\text{H}_{17}\text{ONS}$	280–281	$0.63 \cdot 10^2$	<i>n</i> -Hexane
			279–280	$1.5 \cdot 10^2$	Ethanol
Arylcarbamates	Asulam	$\text{C}_8\text{H}_{10}\text{O}_4\text{N}_2\text{S}$	270	$1.6 \cdot 10^4$	Ethanol
			238	$3.72 \cdot 10^4$	Ethanol
	Betanal	$\text{C}_{16}\text{H}_{16}\text{O}_4\text{N}_2$	262.5	$0.3 \cdot 10^4$	Ethanol
			265	$0.35 \cdot 10^4$	<i>n</i> -Hexane
			278	$0.35 \cdot 10^4$	<i>n</i> -Hexane
	Carbyne	$\text{C}_{11}\text{H}_9\text{O}_2\text{NCl}_2$	277–278	$1.8 \cdot 10^3$	<i>n</i> -Hexane
			285–286	$1.6 \cdot 10^3$	Ethanol
	IFC	$\text{C}_{10}\text{H}_{13}\text{O}_2\text{N}$	237		Ethanol
			275	$0.85 \cdot 10^3$	<i>n</i> -Hexane
	Chlor-IFC	$\text{C}_{10}\text{H}_{12}\text{O}_2\text{NCl}$	282–286		
			240–241	$2.65 \cdot 10^3$	Ethanol
			273	$0.48 \cdot 10^3$	Ethanol
			274	$1.39 \cdot 10^3$	<i>n</i> -Hexane
	Aniline	$\text{C}_6\text{H}_7\text{N}$	230, 280		<i>n</i> -Hexane
			<i>m</i> -Chloroaniline	$\text{C}_6\text{H}_6\text{NCl}$	239.5, 285–286
Phenylurea derivatives	Dosanex	$\text{C}_{10}\text{H}_{13}\text{O}_2\text{N}_2\text{Cl}$	247	$1.05 \cdot 10^4$	Ethanol
			247	$0.2 \cdot 10^4$	<i>n</i> -Hexane
	Diuron	$\text{C}_9\text{H}_{10}\text{ON}_2\text{Cl}_2$	246	$1.6 \cdot 10^3$	Ethanol
			3,4-Dichloroaniline	$\text{C}_6\text{H}_5\text{NCl}_2$	244–245

TLC analysis

Aluminium oxide (activity II), silica gel KCK and Silufol TLC plates were used, with *n*-hexane, *n*-heptane, chloroform, benzene, ethanol, ethyl acetate, carbon

tetrachloride, diethyl ether, light petroleum, acetone and their mixtures as mobile phases.

For the detection of phenylcarbamates and phenylureas, an azo reaction was used. Diazotization was carried out with sodium nitrite solution after preliminary thermal degradation of the pesticide molecules, then the diazo compound obtained was combined with α -naphthol or α -naphthylamine. Coloured reaction products were obtained with 4-aminoantipyrine in the presence of ammonium persulphate $[(\text{NH}_4)_2\text{S}_2\text{O}_8]$ as an oxidant (betanal), or with *p*-dimethylaminobenzaldehyde (asulam, betanal). The sensitivity of determination was 1–10 μg .

Thiocarbamate pesticides were subjected to reaction with bromophenol blue reagent or with *o*-toluidine after N-chlorination (eptam, tillam, yalan). The sensitivity was 0.25–2 μg . For detection of roneet, Dragendorf reagent or sulphuric acid were also used.

Table III gives the optimum conditions for the determination of some combinations.

TABLE III

LIMITS OF DETECTION AND R_F VALUES OF CARBAMATE AND THIOCARBAMATE DERIVATIVES IN THIN LAYERS OF SORBENT

<i>Pesticide</i>	<i>Sorbent</i>	<i>Mobile phase*</i>	R_F <i>value</i>	<i>Minimum determinable amount</i> (μg)
Asulam	Aluminium oxide	E-W (2:1)	0.55	3
Betanal	Aluminium oxide	C	0.4	3
Benleit	Silufol	CCl_4 -E (9:1)	0.6	1
Carbyne	Aluminium oxide	H-C (1:3)	0.5	5
IFC	Aluminium oxide	H-C (1:3)	0.76	10
Chlor-IFC	Aluminium oxide	H-C (1:3)	0.8	10
Aniline	Aluminium oxide	H-C (1:3)	0.62	
<i>m</i> -Chloroaniline	Aluminium oxide	H-C (1:3)	0.71	
Yalan	Silufol	H-D (4:1)	0.54	1
Roneet	Silufol	H-D (4:1)	0.73	2
Tillam	Silufol	H-D (4:1)	0.80	2
Vernam	Silufol	H-D (4:1)	0.82	0.25
Sutan	Silufol	H-D (4:1)	0.87	1
Yalan	Silufol	B-H (9:1)	0.6	1
Roneet	Aluminium oxide	B-H (3:2 or 4:1)	0.55	10

* B = benzene; C = chloroform; CCl_4 = carbon tetrachloride; D = diethyl ether; E = ethanol; H = *n*-hexane; W = water.

GLC analysis

A Tswet-106 gas chromatograph with a thermoionic detector (TID) was used under both isothermal conditions and with temperature programming. The lengths of the glass columns were 1 and 2 m, with I.D. 3 mm.

The stationary phases SE-30 (3 and 5%), XE-60 (5%), DC-550 (5%) and OV-17 (2 and 5%) on Chromaton N AW DMCS and Chromaton N AW (0.16–0.24 mm) were investigated at different temperatures.

The following optimum conditions for the separation of six thiocarbamate pesticides were found: column temperature, 140–170°C; nitrogen flow-rate, 20 ml min⁻¹; compressed air flow-rate, 200–400 ml min⁻¹; hydrogen flow-rate 15 ml min⁻¹; amplification, 5 · 10⁻¹²–100 · 10⁻¹² A.

Table IV gives results for the separation of thiocarbamate derivatives using a TID and 5% DC-550 on Chromaton N AW DMCS and a 5% SE-30–5% XE-60 (1:1) mixed phase.

TABLE IV

SEPARATION OF SOME THIOCARBAMATE DERIVATIVES BY CHROMATOGRAPHY

Pesticide	5% DC-550		5% SE-30 + 5% XE-60 (1:1)	
	Retention time (sec)	Separation factor	Retention time (sec)	Separation factor
Eptam	270		285	
Sutan	348	1.1	348	1.5
Vernam	405	0.4	375	0.6
Tillam	437	0.3	690	2.5
Yalan	712	1.1	750	1.0
Roneet	954	1.3	910	0.7

Air sampling

When applied in agriculture, the derivatives of urea (DCM, diuron and others) and of some carbamates such as betanal, chlor-IFC, carbyne and pirimor occur mainly as aerosols in air in the working zone and thiocarbamates occur as aerosols and vapours simultaneously. Therefore, when studying conditions for air sampling (absorption media, rate of sampling, duration of aspiration), the pesticide volatility, the form of its application (concentrate, emulsion, granulated preparation, etc.), and the method of treatment of agricultural samples must be taken into account. Hence, when sampling aerosols, the filters investigated were AFA-KhA (filtration material: uniform distribution of ultrathin acetylcellulose fibres) and AFA-V (Perchlor vinyl fibre) ash-free filter-papers.

The rate of air aspiration was up to 15 l min⁻¹. For sampling vapours, silica gel KSK, ASK, glass-wool, acetone, *n*-hexane and ethanol in cooling traps were used as absorbents. The sampling rate was 0.2–1 l min⁻¹.

The absorption capacity of the absorption media was tested in model experiments under laboratory conditions; using an experimental aerosol an aspiration rate was selected and the air volume necessary for analysis was determined. When taking samples of airborne volatile pesticides such as vernam and eptam, combined absorbents (successive filters containing liquid absorbents or silica gel) were used.

DISCUSSION

UV spectrophotometry has been applied to the determination of micro-amounts of pesticides in waters, soils, vegetables and some food products. The use of UV spectrophotometry permits the identification of the products of pesticide transformations in living organisms and the environment and provides information on the processes of pesticide photolysis in the biosphere, because the presence of maxima in the UV spectra indicates the capacity of the molecules to be excited and to undergo specific reactions when UV irradiated.

From Table II it can be seen that maxima at 233–255 and 272–280 nm are a peculiarity of the absorption spectra of thiocarbamate derivatives. The absorption spectrum of tetramethylthiourea, with $\lambda_{\max} = 255.5 \text{ nm}$ ($\epsilon = 17,000 \text{ l mol}^{-1} \text{ cm}^{-1}$), is the result of the effect of conjugation between the thiocarbonyl group and free pair of electrons on the adjacent nitrogen atoms. The presence of an intense maximum at 246–247 nm ($\epsilon = 1600\text{--}10,500 \text{ l mol}^{-1} \text{ cm}^{-1}$) is an absorption peculiarity of urea derivatives. The UV spectra of ether arylcarbamate had an intense maximum near 236–241 nm. These maxima are conditioned mainly by the change in the electrons in the aromatic ring. The limit of detection of the pesticides by spectrophotometry is $0.5\text{--}5 \text{ mg m}^{-3}$, as shown in Table II. The sensitivity of the spectrophotometric method thus satisfies the requirements for methods for the analysis of air in working zones, but its practical application is often limited because of the difficulty of the separate determination of the components of some airborne combinations, the maxima of which coincide or are close together.

For establishing the possibility of separating pesticides with similar structures, TLC was examined. The dependence of the chromatographic parameters on the chemical structure of molecular combinations studied and on the sorbent and the mobile phase was investigated. In TLC using *n*-hexane with thin layers of aluminium oxide and silica gel KSK the mobilities of asulam, betanal, benleite, carbyne, IFC, chlor-IFC, yalan, roneet, tillam, vernam and sutan are zero or nearly zero. In chromatography with mobile phases containing *n*-hexane, the R_F value increases as a function of the extent of blocking of the active centres of the adsorbent by the components of the mixture. As chloroform and benzene have specific interactions with the adsorbent, competing with interactions of the adsorbed compounds, the R_F values of pesticides are higher in chloroform and benzene than in *n*-hexane. The R_F values increase considerably when diethyl ether is added to the solvent system, owing to a strong specific interaction between the ether and the adsorbent. The optimum conditions for separating some arylcarbamate derivatives (carbyne, IFC, Chlor-IFC and their aniline and *m*-chloroaniline metabolites) and thiocarbamate derivatives (roneet, tillam, sutan and yalan) were determined. Asulam, betanal and benleite have R_F values of zero or nearly zero under the selected conditions. The detection limit is 0.1 mg m^{-3} (refs. 12–16).

Thiocarbamate derivatives with similar structures, e.g., vernam, sutan and tillam, cannot always be separated and identified reliably. GLC was used for this purpose. The optimum conditions for separating six thiocarbamates were obtained by using a TID with 5% DC-550, 5% XE-60 and mixed 5% SE-30–5% XE-60 (1:1) as the stationary phase. From the data in Table IV, it can be seen that the best separations of sutan and vernam and of vernam and tillam are achieved on the mixed

TABLE V
CONDITIONS OF AIR SAMPLING FOR SOME PESTICIDES

<i>Pesticide</i>	<i>Aggregate state</i>	<i>Adsorbent</i>	<i>Sampling rate (l min⁻¹)</i>	<i>Investigated air volume (l)</i>
Bcnlciit	Aerosol	AFA-KhA	5	200
Carbyne	Aerosol	AFA-KhA	5	20
IFC	Aerosol	AFA-KhA	5	40
Chlor-IFC	Aerosol	AFA-KhA	5	40
DCM	Aerosol + vapour	Ash-free filter paper	5	20
		Acetone	0.3-0.5	10
Vernam	Aerosol + vapour	AFA-KhA + liquid absorber (acetone)	1	1
Roneet	Aerosol + vapour	AFA-KhA	2	10
Tillam	Vapour	Silica gel (or acetone)	0.3-0.4	10
		AFA-KhA	3-5	10
Eptam	Aerosol + vapour	AFA-KhA + liquid absorber (<i>n</i> -hexane)	0.4	10
		AFA-KhA	3-5	10
Yalan	Aerosol	Glass-wool;		
		AFA-KhA	5	10

column, and of tillam and yalan and of yalan and roneet on DC-550. The limits of detection of thiocarbamate pesticides in air are 0.02-0.2 mg m⁻³.

Studies of the air sampling conditions showed that pesticides that occur as aerosols are satisfactorily absorbed by the AFA-KhA and AFA-V ash-free filter-papers. The AFA-KhA filter can be used for vapour sampling when the pesticide concentration is not higher than 5 mg m⁻³. The results showed that when sampling air containing high-volatility pesticides (e.g., vernam and eptam), two or three AFA-KhA filters have to be used when the concentration is higher than 50 mg m⁻³. When the concentrations are higher than 100 mg m⁻³ a control absorbing apparatus with a liquid absorber must be connected in series with the filter holder. Table V lists the conditions of air sampling for some pesticides.

Table VI gives the results of pesticide detection by different methods.

TABLE VI
RESULTS OF DETERMINATION OF SOME PESTICIDES BY DIFFERENT METHODS

Initial concentration: 2 MAC; number of determinations is 6-10; all values are within a 95% confidence limit.

<i>Pesticide</i>	<i>Recovery (%)</i>		<i>Pesticide</i>	<i>Recovery (%)</i>	
	<i>UV spectro-photometry</i>	<i>TLC</i>		<i>TLC</i>	<i>GLC</i>
Betanal	91 ± 5.5	90 ± 5	Vernam	89 ± 10.8	90 ± 2.5
Carbyne	97.2 ± 3.5	94 ± 11	Sutan	70.2 ± 5.5	84.5 ± 4.8
IFC	89.8 ± 3.9	89 ± 13.9	Roneet	87 ± 5	88.5 ± 3.4
Chlor-IFC	94.5 ± 4.0	90 ± 12.5	DCM	88 ± 11.5	92 ± 5.6

In conclusion, it appears that the individual pesticides in air can be detected by UV spectrophotometry with high sensitivity. TLC and GLC are effective in separating mixtures, and the combination of these methods makes it possible for the investigated compounds to be identified.

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