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ISOTACHOPHORESIS OF CATIONIC HERBICIDES IN WATERS AND SOILS

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SUMMARY

A method for the determination of quaternary cationic herbicides (diquat and paraquat) and triazine herbicides in water and soil extracts by capillary isotachophoresis is proposed. More basic triazines (atratone, prometryne, etc.) can be determinated directly using enforced isotachophoresis. Very weak triazine bases (atrazine, simazine, etc.) have to derivatized by nucleophilic substitution of chlorine by electron-donor (*e.g.*, OCH_3) or quaternary ammonium groups. Recoveries from soils are 70–80% of quaternary and 90–95% of triazine herbicides. The limit of determination with both the types of herbicides is about 10 μg/kg of sample.

INTRODUCTION

The possibility of determining the growth regulator chlormequat (CCC), the quaternary cationic herbicides diquat and paraquat and the slightly basic triazine herbicides atrazine, simazine, atratone, prometryne, desmetryne and methoprotryne in water and soil extracts by capillary isotachophoresis has been studied. For the determination of these compounds, various methods have been proposed.

The determination of I after isolation and purification is mostly performed spectrophotometrically by measuring the coloured ion associate with dipicrylamine extracted into dichloromethane[1,2]. The optimal procedure for determination was established by measuring ^{14}C-labelled samples[3]. Cationic herbicides of the paraquat type were determined spectrophotometrically after reduction to the half-reduced semiquinoid cation radical[4,5], by gas chromatography[5–7] after pyrolysis[6] or catalytic hydrogenation[7] of quaternary cations and by liquid chromatography, mostly reversed-phase[8,9]. The possibility of very sensitive determination is also offered by differential pulse polarography[10]. The isolation and pre-concentration of quaternary cations from water and soil samples are carried out on cation exchangers in the H^+ or Na^+ form[4–5]. In soils cationic herbicides are very strongly bonded, even to organic matter, and for their release it is necessary to decompose the sample with *ca.* 50% sulphuric acid[4].

Triazine herbicides and their residues have most often been determined by gas chromatography[11–15]. Liquid chromatography, however, seems to be more suit-

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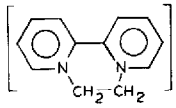
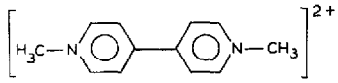
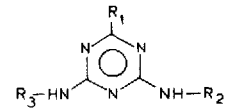
I	Chlormequat, CCC	$[ClCH_2CH_2N(CH_3)_3]^+$
II	Diquat	
III	Paraquat	
IV–XII	*s*-Triazines	
IV	Atrazine	$R_1 = Cl$; $R_2 = C_2H_5$; $R_3 = i\text{-}C_3H_7$
V	Simazine	$R_1 = Cl$; $R_2,R_3 = C_2H_5$
VI	Atratone	$R_1 = OCH_3$; $R_2 = C_2H_5$; $R_3 = i\text{-}C_3H_7$
VII	Simetone	$R_1 = OCH_3$; $R_2,R_3 = C_2H_5$
VIII	Prometryne	$R_1 = SCH_3$; $R_2,R_3 = i\text{-}C_3H_7$
IX	Desmetryne	$R_1 = SCH_3$; $R_2 = CH_3$; $R_3 = i\text{-}C_3H_7$
X	Methoprotryne	$R_1 = SCH_3$; $R_2 = i\text{-}C_3H_7$; $R_3 = (CH_2)_3OCH_3$
XI	(4-Ethylamino-6-isopropylamino-*s*-triazin-2-yl)trimethylammonium	$R_1 = \overset{+}{N}(CH_3)_3$; $R_2 = C_2H_5$; $R_3 = i\text{-}C_3H_7$
XII	(4,6-Bisethylamino-*s*-triazin-2-yl)trimethylammonium	$R_1 = \overset{+}{N}(CH_3)_3$; $R_2,R_3 = C_2H_5$

able[16–19] because it allows the analysis even of metabolites without derivatization[20]. For qualitative and quantitative analyses, methods based on inhibition of the Hill reaction are used, often connected with thin-layer chromatography[21] or various bioassays[22,23] and radioimmunoassay[24] methods, for both types of herbicides. Extraction with various solvents, most often with chlorinated hydrocarbons[15,25], or adsorption on styrene–ethylene glycol dimethacrylate copolymer[26] have been recommended for the isolation of triazine herbicides from water. A mixture of acetonitrile with 10% of water[20,25,27] or methanol[28] is most often used for the elution of triazines from soils.

Isotachophoresis is very advantageous for the final determination of cationic and basic herbicides, as the number of possible interferent compounds is much smaller than in gas (GC) or high-performance liquid chromatography (HPLC). The great number of neutral organic compounds that are extracted with organic solvents, especially from soil samples, makes it necessary to include in the isolation procedure for GC or HPLC determinations other operations, *e.g.*, re-purification on an aluminium oxide column[28], chemical transformation[6,7] or derivatization[14]. The possible simplification of the isolation procedures was therefore the reason why we chose isotachophoresis (ITP) for the determination.

EXPERIMENTAL

For model studies, standards (triazines; Ciba-Geigy) or compounds isolated and purified from commercial formulations were used as samples. Quaternary cation

perchlorates of I, II and III were precipitated from commercial formulations with sodium perchlorate solution, recrystallized from deionized water and dried over P_2O_5 under vacuum.

VI and VII were prepared by boiling IV and V (1 mmol), respectively, for 2 h with sodium methoxide (2.1 mmol) in methanol. After dilution with water, neutralization and partial evaporation, the deposited products were recrystallized from water or aqueous ethanol and dried over P_2O_5 under vacuum.

Quaternary chlorides of (4,6-bisalkylamino-*s*-triazin-2-yl)trimethylammonium were prepared by the reaction of 2-chloroderivatives with trimethylamine. A saturated solution (1 mmol) of the 2-chloro derivative (*e.g.*, IV) in benzene was mixed with 3 ml of trimethylamine solution of concentration 1.5 mol/l in benzene (4.5 mmol) and the reaction mixture was allowed to evaporate freely. The total solids were recrystallized from anhydrous ethanol and dried over P_2O_5 at 60°C under vacuum. The purity was monitored by elemental analysis.

Methanol was purified by fractional distillation, chloroform by distillation and benzene after drying with sodium by distillation. Acetonitrile (UCB) and dichloromethane (Loba) were used without purification.

Determination of II or III in water

To 1 l of water containing 10–1000 μg of bivalent cation, 3 ml of a 10^{-2} mol/l solution of sodium dodecylsulphate and 20 ml of reduction solution (5% $Na_2S_2O_4$ in 3 mol/l NaOH) were added. The blue ion associate of the cation radical formed with the dodecylsulphate was extracted with two 10-ml volumes of dichloromethane. The separated organic layers were evaporated to dryness, 1 ml of leading electrolyte containing 25% of methanol was applied for dissolution and 10 or 25.9 μl were injected for ITP analysis. The results were monitored in parallel by spectrophotometric determination with evaluation by means of the corrected absorbance[4].

Determination of II or III in soil

To 100 g of soil containing 2.98% of organic matter (chromic acid titration method), 50 ml of an aqueous solution of herbicide containing 0.2, 2.0 and 20.0 mg/l of bivalent cation was added. The suspension, with occasional stirring, was dried at 105°C to roughly the original weight. Isolation from the soil was performed by the method described[5] with concentration on Dowex 50-X8 (Na^+). The eluate (35 ml) in concentrated NH_4Cl solution was collected and diluted to 50 ml. To 25 ml of this solution 0.5 ml of 10^{-4} *M*, 0.5 ml of 10^{-3} *M* or 5 ml of 10^{-3} *M* sodium dodecyl sulphate solution (depending on the amount of herbicide in the soil) and 6 ml of a fresh solution of 1% $Na_2S_2O_4$ in 1 *M* NaOH were added and the extraction was carried out with two 5-ml volumes of dichloromethane. The combined blue organic layers were evaporated, the total solids dissolved in 1 ml of water and 25.9 μl were used for ITP analysis.

Determination of distribution ratios of ion associates

To 10 ml of a $4 \cdot 10^{-5}$ mol/l aqueous solution of II or III, 1, 2, 4 and 10 ml of $2 \cdot 10^{-3}$ mol/l of sodium dodecylsulphate solution were added and the volume was made up to 20 ml with water. The solutions were extracted with 20 ml of dichloromethane, the organic layer was evaporated, the residue dissolved in 1 ml of water

and 25.9 μl of the aqueous solution were taken for ITP analysis (system B for II, system C for III). The content of herbicide remaining in the aqueous layer was determined in parallel by UV spectrophotometry. The absorbance was measured at 308 nm for II and at 256 nm for III against the blank. Water extracted with dichloromethane was used as the blank.

Determination of triazine herbicides in water

The triazines were isolated by a procedure analogous to those procedures described elsewhere[15,25]. Water (1 l) was taken, the pH was adjusted to *ca.* 8 and extraction was carried out with three 30-ml volumes of chloroform. The combined organic layers were evaporated to a small volume and dried in a conical cell with a ground-glass joint using a flow of air or nitrogen. The residue was dissolved (preferably overnight) in 1 ml of methanol–10^{-2} *M* HCl (1:3) and then injected.

This procedure is suitable for the determination of more basic triazines (atratone or prometryne types). 2-Chlorotriazines (atrazine type) have to be converted into more basic derivatives by means of the two following procedures.

(a) To the residue in a conical cell were added 3 ml of a fresh solution of sodium methoxide (0.01 mol/l) and the sample was heated for 2 h under reflux. The solution of the derivative (*e.g.*, VI) was evaporated to dryness in a flow of nitrogen and the residue was dissolved in 1 ml of methanol–$4 \cdot 10^{-2}$ *M* HCl (1:3). A 25.9-μl volume of the solution was taken for ITP analysis.

(b) The residue in the conical cell was dissolved in 2 ml of benzene and, after the addition of 1 ml of a 0.1 *M* solution of trimethylamine in benzene, the mixture formed was freely evaporated. The product was dissolved in 1 ml of water and 25.9 μl of this solution were used for ITP analysis.

Determination of triazine herbicides in soil

To 100 g of soil (2.98% organic matter), 50 ml of acetone solution containing 0.05, 1.0 and 20.0 mg/l of herbicide (IV, VI, VIII and IX were chosen as model compounds) were added and the solvent was evaporated with continuous stirring at the room temperature. The sample was eluted twice with 200 ml of boiling solvent and finally washed on a sintered-glass disk with 100 ml of the solvent. Anhydrous methanol[28] or acetonitrile–water (9:1)[20,27] were used as solvents. For the highest concentration of herbicide (*ca.* 10 mg/kg) only 10 g of soil were taken for the procedure and elution was performed with a ten times smaller amount of solvent. The combined filtrates were evaporated to dryness, the residue was dissolved in 3 ml of chloroform and the solution was evaporated again in a conical cell equipped with a ground-glass joint in a flow of air or nitrogen. The subsequent procedure was the same as for water analysis.

Equipment and ITP operational systems

The determinations were carried out on an instrument for capillary isotachophoresis with coupled columns. A pre-separation capillary (220 × 0.75 mm I.D.) served for the separation of the large amounts of accompanying ions (especially Na^+). The current was set to 200 μA. With the analytical capillary (250 × 0.3 mm I.D.) the current was 50 μA. Zone lengths were measured using an electronic stopwatch from the derivative record of the conductivity detector signal and when there

TABLE I

OPERATIONAL SYSTEMS USED

System	*Substance*	*Leading ion c(mol/l)*	*Counter ion*	*pH*	*Additive*	*Terminating electrolyte c(mol/l)*	*pH*
A	CCC	K^+ 10^{-2}	Acetate	4.7–5.4	0.05% PVA	$Tris^+$–acetate 5.10^{-3}	5.0
B	Diquat	K^+ 10^{-2}	Citrate	6.0	0.05% PVA	$Tris^+$–acetate 5.10^{-3}	5.8
C	Paraquat	K^+ 10^{-2}	Diidotyrosinate	7.4	0.05% PVA	$Tris^+$–acetate 5.10^{-3}	7.0
D	*s*-Triazines	K^+ 10^{-2}	Acetate	5.08	0.05% PVA	Glycine 2.10^{-2}	≈5.0

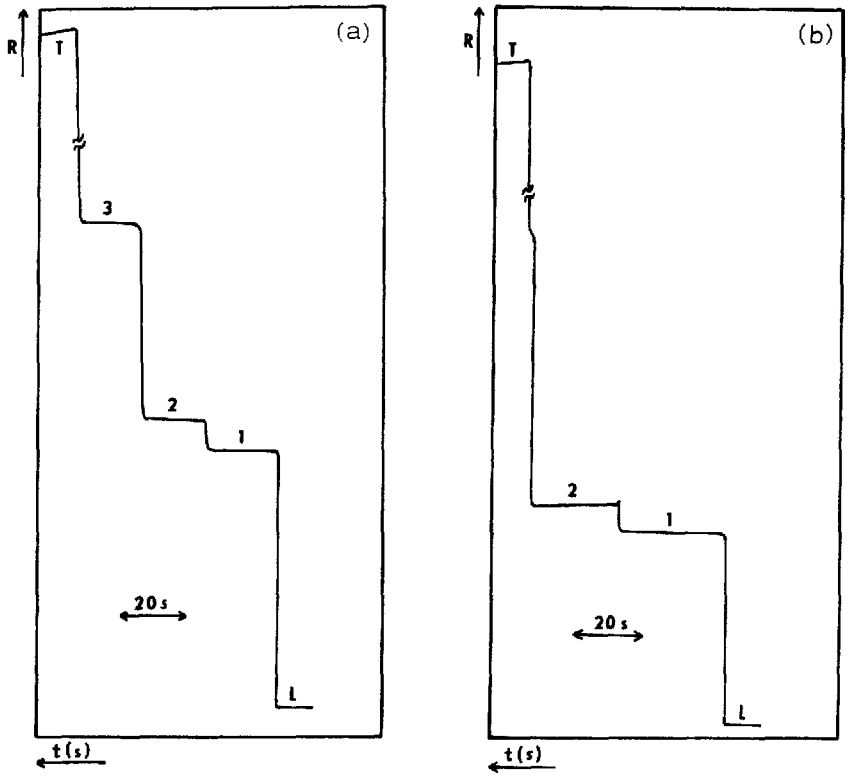


Fig. 1. Separation of quaternary ions. (a) Operational system C. Injection of 1 μl of mixture containing 5 mmol/l of II and III and 10 mmol/l of I. 1 = Mixed zone of II and Na^+; 2 = III; 3 = I. (b) Operational system B. Injection of 1.5 μl of mixture containing 5 mmol/l of II and 15 mmol/l of Na^+. 1 = Na^+; 2 = II.

TABLE II

CONTENT OF ACTIVE COMPOUNDS IN COMMERCIAL FORMULATIONS

Formulation	*Density* ($g\ cm^{-3}$)	*Concentration*		*Relative standard deviation (%)*
		Declared	*Found*	
Retacel I (CCC)	1.126	55%	56.6%	0.88
Retacel II (CCC)	1.124	55%	55.2%	0.57
Reglone I (diquat)	1.208	200 g/l	302.9 g/l	1.93
Reglone II (diquat)	1.203	200 g/l	285.6 g/l	1.26
Gramoxone I (paraquat)	1.087	200 g/l	318.1 g/l	2.43
Gramoxone II (paraquat)	1.103	200 g/l	294.7 g/l	1.06

were a large number of zones, they were screened on the CRT display. Samples were injected using a Hamilton microsyringe (10 μl) or with a dosing valve of inner volume 25.9 μl.

The compositions of the optimized operational systems for the determination of different analytes are given in Table I.

RESULTS

Fig. 1a shows the isotachophoretic separation of a model mixture of growth regulator I and quaternary herbicides II and III in system C. In this system, however, the bivalent cation of II forms a mixed zone with Na^+. For the determination of II it was therefore necessary to choose system B (Fig. 1b).

Capillary isotachophoresis can also be used as a rapid method for monitoring the composition of commercial formulations (Table II). Unexpectedly large differences between the declared and found contents of both herbicides were confirmed even by potentiometric determination with coated-wire indicator electrodes[29].

Table III gives the results of the determination of II and III in water and Table IV gives the results of the determination of III in soil. Fig. 2 is a record of the III zone after isolation from soil containing 96.2 μg/kg of herbicide, in comparison with the zone of a standard sample corresponding to 100% recovery.

TABLE III

DETERMINATION OF QUATERNARY HERBICIDES IN WATER

Analysis of potable water with additions of 10, 100 and 1000 μg of bivalent cation to 1 l of water. Injected 25.9 μl of the sample concentrated in ratio 1:1000. Mean of 3 parallel determinations.

Herbicide	*Given* ($\mu g/l$)	*Found* ($\mu g/l$)	*R.S.D.* (%)	*Recovery* (%)
Diquat	10	7.9	16.3	65– 90
	100	95.8	4.2	92– 98
	1000	976	2.8	95–100
Paraquat	10	8.8	14.1	75– 95
	100	94.9	3.6	92– 97
	1000	981	3.1	94–102

TABLE IV

DETERMINATION OF PARAQUAT IN SOIL

Analysis of soil with additions of 0.1, 1.0 and 10 mg/kg of paraquat. The sample was injected by stopcock (25.9 μl). Mean of 3 parallel determinations. The results were compared with the values of the spectrophotometric determination[5].

Given (mg/kg)	*Weight of sample (g)*	*Found ITP (mg/kg)*	*R.S.D. (%)*	*Mean recovery (%)*	*Found spectrophotometrically (mg/kg)*	*R.S.D. (%)*	*Mean recovery (%)*
0.0962	100	0.0711	8.5	73.9	0.066*	12.6	68.7
1.011	50	0.810	6.2	80.1	0.738	7.4	73.0
9.785	10	7.65	5.0	78.2	7.47	4.0	76.3

* Spectrophotometry of extracted ion associate in dichloromethane.

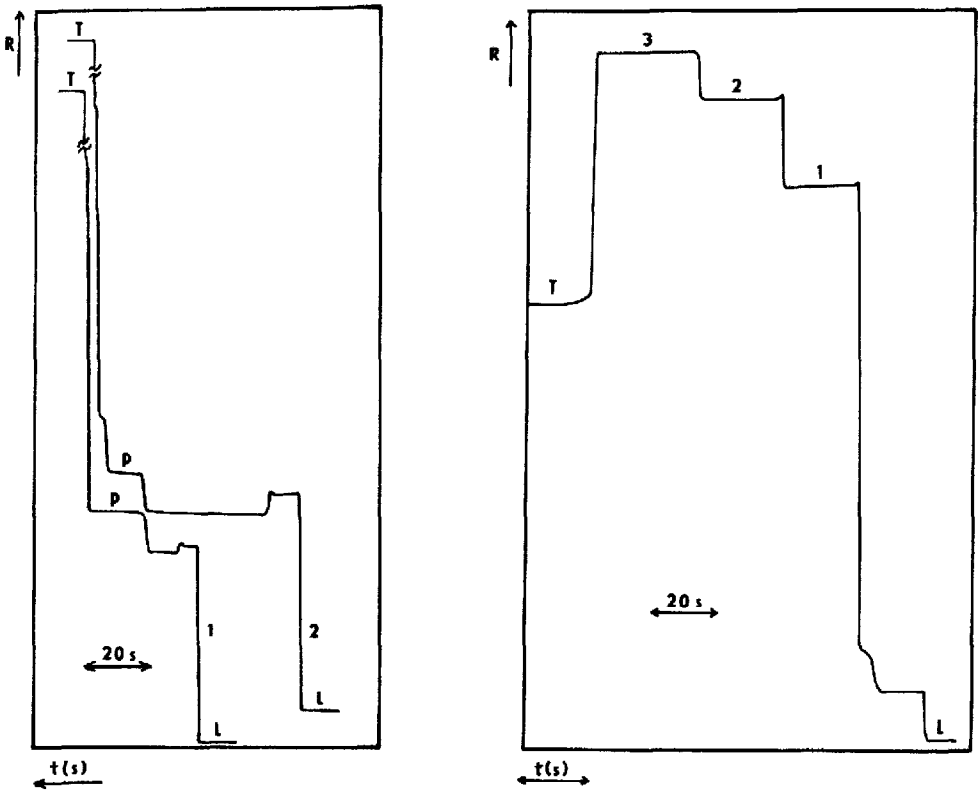


Fig. 2. Determination of paraquat in soil. Operational system C. 1, Injection of 25.9 μl of solution containing 10 mg/l of cation; 2, injection of 25.9 μl isolated from 100 g of soil containing 96.2 μg/kg of cation (extracted into 1 ml of water). P = III zone.

Fig. 3. Separation of triazine herbicides in operational system D. Injection of 4 μl of mixture of concentration 10^{-3} mol/l of each component. 1 = VI; 2 = IX; 3 = X.

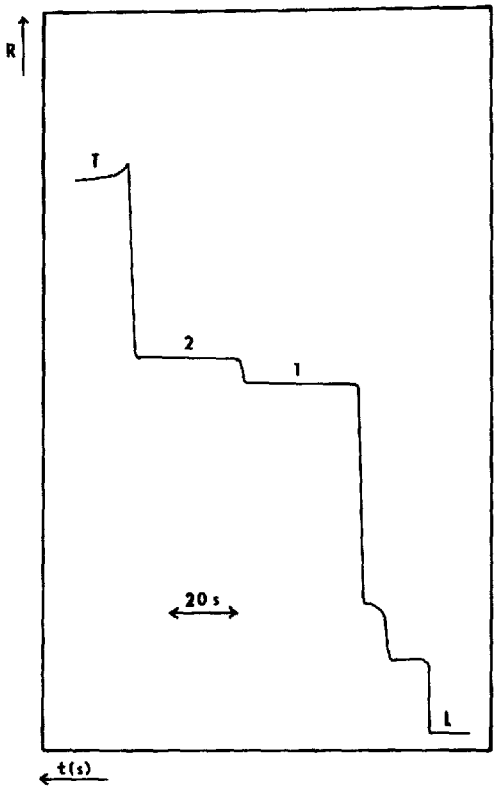


Fig. 4. Separation of chlorotriazine derivatives in operational system D. Injection of 5 μl of mixture containing 1.65 μg of both components. 1 = XII; 2 = XI.

The isotachophoretic behaviour and the separation of more basic triazine herbicides are illustrated in Fig. 3 and the separation of trimethylammonium derivatives (XI and XII) of very weakly basic chlorotriazines is shown in Fig. 4. Calibration graphs for some *s*-triazines are shown in Fig. 5.

Table V gives the results of the determination of triazine herbicides in soil.

DISCUSSION

The determination of the I by isotachophoresis is suitable only for commercial formulations. For its sensitive determination in waters and soils we did not succeed in finding a pre-concentration technique that is simpler than present purification and pre-concentration procedures[1,2].

The isotachophoretic behaviour of the cationic herbicides II and III is of interest. In potassium acetate–acetic acid (pH 4.7–5.4)–Tris operational systems the effective mobilities of both bivalent cations are only slightly higher than the mobility of the leading ion. The use of larger samples at a given separation capacity leads to the formation of mixed zones not only with both herbicides but even with the leading ion. A decrease in the effective mobility of bivalent herbicides can be obtained with a higher charge of the counter ion[30] or by the formation of an ion associate. These

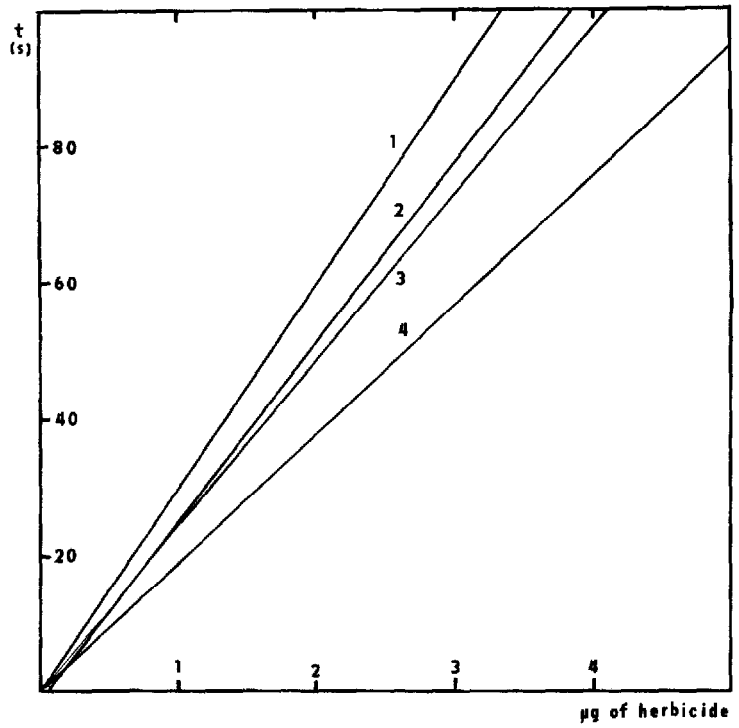


Fig. 5. ITP calibration lines. Operational system D. 1 = IX; 2 = X; 3 = VIII; 4 = XI (1 μg of derivative corresponds to 0.785 μg of IV).

TABLE V

DETERMINATION OF TRIAZINES IN SOIL

Analysis of soils with 0.025, 0.5 and 10 mg of herbicide in 1 kg of sample. Injected, 25.9 μl of concentrated eluate. Results are a mean of 3 parallel determinations (for prometryne and atrazine of 8 determinations). A = atrazine converted to atratone; B = atrazine converted to trimethylammoniumderivative.

Herbicide	*Weight of sample (g)*	*Given (μg/kg)*	*Found (μg/kg)*	*Recovery (%)*	*R.S.D. (%)*
Prometryne	100	24.8	21.9	88.3	16.3
	50	498	465	93.4	6.2
	10	9630	8930	92.7	3.6
Desmetryne	100	25.4	21.7	85.4	28.3
	50	486	436	89.7	8.9
	10	9891	9280	93.8	5.1
Atratone	100	25.5	23.3	91.4	22.1
	50	531	512	96.4	7.5
Atrazine A	50	482	368	76.4	22.4
	10	10,894	9400	86.3	18.2
Atrazine B	50	482	430	89.2	10.9
	10	10,894	10,195	93.6	6.0

TABLE VI

DISTRIBUTION RATIOS OF ION ASSOCIATES OF DIQUAT AND PARAQUAT WITH DODECYL SULPHATE BETWEEN DICHLOROMETHANE AND WATER

The distribution ratio was determined by the extraction of $2 \cdot 10^{-5}$ mol/l herbicide solution.

Molar ratio, herbicide: dodecylsulphate	*Distribution ratio*			
	Diquat		*Paraquat*	
	ITP	*UV spectrophotometry*	*ITP*	*UV spectrophotometry*
1:5	0.56	0.56	0.48	0.50
1:10	1.93	1.89	1.80	1.86
1:20	4.08	3.98	3.17	3.31
1:50	3.08	3.13	2.39	2.42

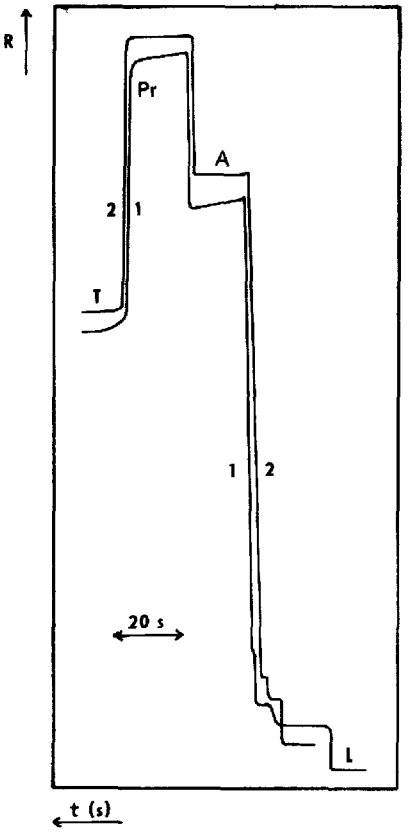


Fig. 6. Determination of triazines in soil. System D. 1, Injection of 25.9 μl isolated from 100 g of soil containing 265 μg/kg of VI and 249 μg/kg of VIII; 2, injection of 25.9 μl of solution containing 25 mg/l of standards (corresponds to 250 μg/kg at 100% recovery). A, VI zone; Pr, VIII zone.

effects are used in operational systems B and C. Use of the large organic anion 3,5-diiodotyrosinate as the counter ion decreases the effective mobility of III to a value lower than that of Na^+.

We have found that the formation of ion associates could also be used for the concentration of quaternary herbicides from aqueous solution. Ion associates of bivalent cations are not completely extractable into organic solvents (Table VI). The distribution ratios are too low for satisfactory isolation. However, the stable ion associates formed between dodecyl sulphate and the semi-reduced cation radical of II or III can be extracted almost quantitatively by one-step extraction (the distribution ratio is about 400 for both herbicides). This fact simplifies especially the determination of herbicides in waters where extraction can replace the concentration on an ion exchanger[4,5], and thus it increases the sensitivity of both isotachophoretic and spectrophotometric determinations to the 10 μg/l level. The isotachophoretic determination, however, is more reproducible. The spectrophotometric determination has the disadvantage of easy re-oxidation of the cation radical, which occurs during the measurement and decreases the precision of the method. For the determination of quaternary herbicides in soils such a simplification is not possible because boiling of soil with 50% sulphuric acid is necessary and the extract formed cannot be used for direct ITP determination or for cation radical extraction.

The isotachophoretic behaviour of triazine herbicides with OCH_3 and SCH_3 groups is an example of enforced isotachophoresis[31], where even a large number of zones with inverted mobilities (Figs. 3 and 6) behaves correctly and can be analytically exploited (Fig. 5). An inseparable pair in system D is represented by VIII and X. VIII and IX show a tendency to form mixed zones although their relative step heights differ sufficiently.

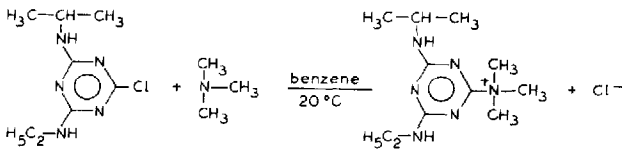
Slightly basic triazines (2-chlorotriazines) with pK_a values of less than 2[20,32–34] cannot be determined directly by ITP. The great reactivity of the chlorine atom allows an easy substitution to be performed, however. We tried two conversions that give quantitative yields of derivatives:

$$\text{T-Cl} + \text{CH}_3\text{O}^- \rightarrow \text{T-OCH}_3 + \text{Cl}^-$$

and

$$\text{T-Cl} + \text{N(CH}_3)_3 \rightarrow \text{T-}\overset{+}{\text{N}}\text{(CH}_3)_3 + \text{Cl}^-$$

Derivatization producing quaternary ammonium salts seems to be more suitable:



IV XI

The advantage lies in the simple preparation procedure and in the possibility of separating derivatives XI and XII, which differ in the homologue increment (Fig. 4). In contrast, VI and VII form a mixed zone in system D.

TABLE VII

DEPENDENCE OF RECOVERY ON THE TREATMENT OF SAMPLE

The conditions are the same as in the Table V. The experiments were performed at the highest concentration level. B = analyzed after conversion to trimethylammoniumderivative.

Herbicide	*Coated from*	*Macerated by*	*Recovery (%)*	*Recovery total (%)*
Prometryne	Water	Methanol	89.9	92.7
	Acetone	Methanol	91.7	
	Water	Acetonitrile (90%)	94.2	
	Acetone	Acetonitrile (90%)	95.3	
Atrazine B	Water	Methanol	85.1	93.6
	Acetone	Methanol	97.9	
	Water	Acetonitrile (90%)	88.8	
	Acetone	Acetonitrile (90%)	101.6	

In addition to the mode of derivatization (Table V), the recovery of triazines depends on a number of factors relating to the isolation procedure. With a more detailed treatment of the results, it was revealed that the choice of the solvent used for the release of triazines from soil and, with IV, even the method of coating on the model sample, were of statistical significance. The soils were coated by VIII and IV both from acetone and from aqueous solution (0.001 *M* HCl). The samples prepared from aqueous solutions were dried to approximately the original weight at 60°C. IV is partially decomposed and hydroxyatrazine is formed, which was always found in small amount by ITP in samples prepared from aqueous solutions. Therefore, the yields of the derivative are smaller from "aqueous" solution coatings (Table VII). With the drying and treatment of soil samples with atrazine it is necessary to consider

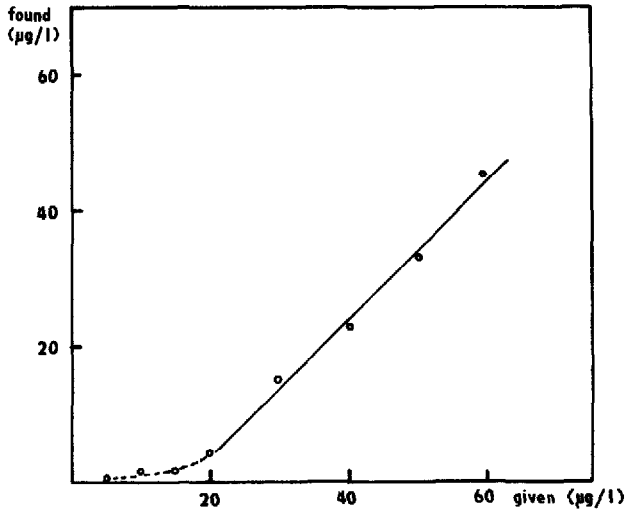


Fig. 7. Dependence of prometryne recovery from waters on concentration. Analysis of 1 l of potable water with addition of 0.5, 1.0, 1.5, 2.0, 3.0, 4.0, 5.0 and 6.0 ml of solution of VIII containing 10 mg/l of the standard.

this possibility, as was demonstrated in a paper devoted to the problem of ageing of samples on storage[27]. The method of herbicide coating with VIII is not of statistical significance.

In the determination of triazines in waters where, at the given sensitivity of the method, they could be measured at the μg/l level, we have experienced difficulties in the determination of the lowest concentrations. Triazines can be quantitatively extracted from a threshold value of about 15 μg/l (Fig. 7). The problem will be investigated further.

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