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Note

Simultaneous determination of active ingredient and chlorophenol impurities in phenoxy acid herbicide formulations by high-performance liquid chromatography with ultra-violet and electrochemical detection

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Official methods for the determination of phenoxy acid herbicides in formulations have been based on volumetry, infrared spectrophotometry or gas–liquid chromatography (GLC)[1,2]. The GLC methods include derivatization of the acids to render them volatile, a step which may not always be reproducible. In recent years high-performance liquid chromatography (HPLC) has been introduced for the analysis of phenoxy acid herbicides, *e.g.*, refs. 3–5. Here we present an HPLC method with UV-detection for the analysis of the active ingredient in formulations of 2,4-D (2,4-dichlorophenoxyacetic acid), MCPA (2-methyl-4-chlorophenoxyacetic acid), dichlorprop (2,4-dichlorophenoxypropionic acid) and mecoprop (2-methyl-4-chlorophenoxypropionic acid). This method has been used for the analysis of hundreds of samples during the last 7 years.

Chlorophenols, which occur in these formulations at a level of about 1%, are toxic compounds and should be controlled. They have been selectively analyzed by HPLC with electrochemical detection[6]. By coupling UV and electrochemical detectors in series we have achieved a simultaneous determination of the active ingredient of phenoxy acid herbicide formulations and of the chlorophenol impurities.

EXPERIMENTAL

A Spectra-Physics Model 3500B liquid chromatograph (Spectra-Physics, Santa Clara, CA, U.S.A.) was used. It was equipped with a Valco injector, 10-μl loop and a UV detector (Spectra-Physics SP8200) operated at 280 nm having a cell volume of 20 μl. A Biosciences electrochemical detector (TL-4-Thin layer Detector cell and LC-4 Control Unit; Bioanalytical Systems, West Lafayette, IN, U.S.A.) was connected in series with the UV-detector. It was kept in a Faraday cage (an empty can) to minimize noise. The electrode paste was CP-W, and it was run at +1.05 V. The column was of stainless steel, 25 cm × 4.6 mm I.D., packed with Spherisorb ODS, 5 μm. The eluent was methanol A.R.–0.1 *M* acetic acid, 45:55 to 55:45 depending on the composition of the formulation. A SMI Micro/pettor® (SMI, Berkeley, CA, U.S.A.) was used for pipetting liquid formulations. Reference substances were kindly provided by Bayer, Leverkusen, G.F.R.

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One hundred μl of liquid formulation, pipetted with the Micro/pettor®, or 5–10 mg of powder were carefully dissolved in eluent. The solution was made up with eluent to a volume giving well defined peaks of the active ingredients within the linear range of the chromatographic system, usually 100 ml. Standard solutions were prepared in the same way. Each sample was injected twice between injections of standard solutions of active ingredient. Standard solutions of chlorophenols were injected intermittently. Peak heights were used for calculations.

RESULTS AND DISCUSSION

HPLC was chosen for the determination of the active ingredient (a.i.) in formulations primarily because of its simplicity and reliability. Especially in the case of non-volatiles, such as phenoxy acids formulated as salts, HPLC is preferred to GLC since no derivatization with toxic alkylating agents, nor laborious handling of the material is involved. Furthermore, reproducibility is very good. In early studies an internal standard solution, 2-chlorophenol in the eluent, was used for dissolving the samples. This was found superfluous and was later omitted. Guidelines for tolerances for herbicide formulations are given by FAO[7]. For declared percentages of a.i. in formulations of 50% or higher, the acceptable limits are ±2.5 units (*i.e.*, ±25 g/kg or g/l). The corresponding figures for a.i. contents of 25–50% and 10–25% are ±5% of a.i. and ±6% of a.i. respectively. These tolerances are set because of difficulties likely to be encountered in manufacture and analysis. With the present method 92 samples of the four phenoxy acids, formulated as sodium, potassium or amine salts, have been run in duplicate, see Table I. The mean of the deviation from average between duplicates was ±3 g/l for formulations of 500 g/l or more. For formulations of less than 500 g/l the mean of the deviation from average between duplicates was ±0.8%.

The reliability of the procedure was investigated for twelve samples containing MCPA or mecoprop which were analysed at Kemikaliekontrollen, Denmark, by a GLC method which was routinely used in their laboratory. The method included addition of an internal standard and derivatization with boron trifluoride–methanol. The results of this collaborative study are shown in Table II. The HPLC values are means of duplicate and the GLC values are means of triplicate analyses. The agreement between the two methods is good, the mean difference being 0.4% of a.i. and the maximum difference 1.2%.

TABLE I

DEVIATION FROM AVERAGE OF DUPLICATE ANALYSES OF PHENOXY ACID HERBICIDE FORMULATIONS

Type of formulation	*Number of herbicides in the formulation*	*Active ingredient (a.i.) content of each herbicide*	*Deviation from average, % of a.i. content*		
			Mean	*S.D.*	*n*
Liquid	1	500–800 g/l	±0.5	0.4	49
Powder	1–2	250–750 g/kg	±0.4	0.3	22
Liquid	2–3	100–400 g/l	±0.8	1.1	50

TABLE II

DETERMINATION OF ACTIVE INGREDIENT CONTENT BY TWO LABORATORIES USING DIFFERENT METHODS

Sample No.	*Formulation*	*Content of active ingredient*	
		HPLC, lab. A	*GLC, lab. B*
1	MCPA, powder	685 g/kg	688 g/kg
2		709 g/kg	707 g/kg
3		784 g/kg	783 g/kg
4	MCPA, liquid	716 g/l	721 g/l
5		714 g/l	714 g/l
6		742 g/l	733 g/l
7		718 g/l	715 g/l
8		722 g/l	720 g/l
9		752 g/l	747 g/l
10	Mecoprop, liquid	575 g/l	576 g/l
11		571 g/l	572 g/l
12		606 g/l	608 g/l

Laboratories: A, Uppsala, Sweden; B, Kemikaliekontrollen, Denmark.

Only small amounts of the formulations were used for the analysis. The samples are then easy and safe to handle. One must be aware of the risk of unrepresentative samples when using only 5–10 mg of powder, but the variance between the duplicates and the general agreement obtained in the collaborative study (*cf.*, Tables I and II) indicate that the amounts used were satisfactory. For liquid formulations the Micro/pettor® was used. It operates on the principle of a syringe. A PTFE-sealed stainless-steel plunger operates within a disposable glass capillary. There is no air interface between plunger and liquid, and all liquid, regardless of viscosity, is swept out of the capillary. This enables highly accurate pipetting and makes weighing and determination of specific weights unnecessary. Again, Tables I and II show that pipetting is reliable.

Armentrout *et al.*[6] analysed chlorophenols by HPLC with electrochemical detection. The chlorophenols are easily oxidized at the detector electrode whereas phenoxy acids are not. Fig. 1 gives the extent of oxidation of some compounds at different potentials. A potential of + 1.05 V was chosen to minimize the signal from the phenoxy acids while still retaining a good sensitivity for chlorophenols. Chromatograms of a mixture of phenoxy acids with 0.5% of chlorophenols, determined simultaneously by UV and electrochemical detection, are shown in Fig. 2. Capacity factors for the phenoxy acids and chlorophenols are given in Table III.

The determination of chlorophenols in presence of an excess of phenoxy acids could also be achieved with UV-detection in an eluent with pH 5.0. In the present method with an eluent of pH around 2, the phenoxy acids, having pK_a around 3, are chromatographed in their unionized form. When changing the eluent pH to 5, the acids are ionized and have less affinity for the non-polar column. Thus they are eluted before the phenols. The chlorophenols are, however, more sensitive towards electrochemical detection than UV-detection. Thus, when using the UV-detector only, two separate sample preparations in addition to two separate chromatographic runs have to be made in order to detect low concentrations of chlorophenols. The simultaneous

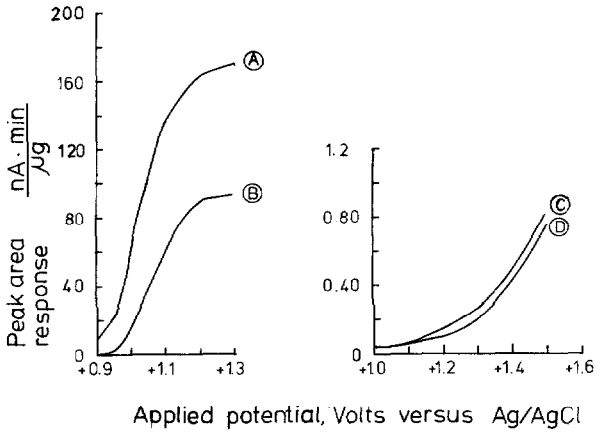

Fig. 1. Relationship between electrochemical detector response and applied potential curves: A, 2,6-dichlorophenol; B, 2-chlorophenol; C, mecoprop; D, dichlorprop.

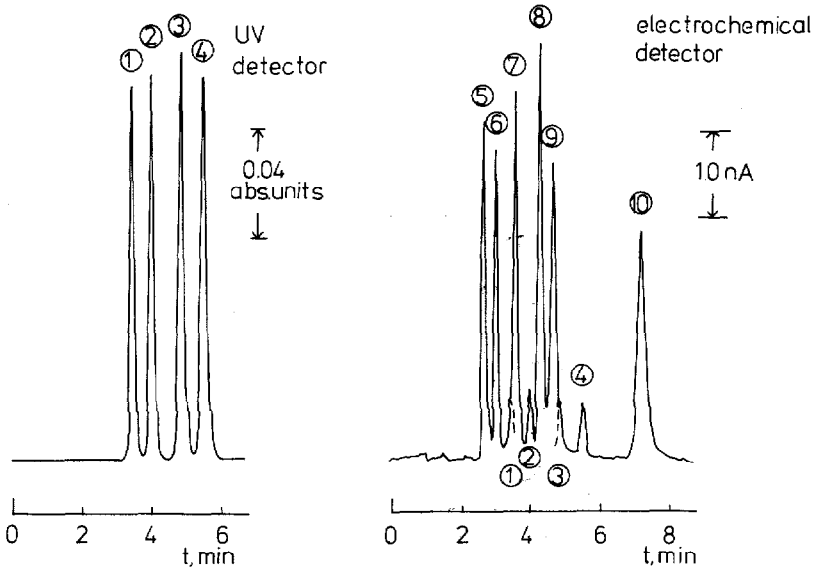

Fig. 2. Chromatograms of a mixture of phenoxy acid herbicides and chlorophenols. Peaks: 1 = 2,4-D, 435 mg/l; 2 = MCPA, 632 mg/l; 3 = dichlorprop, 711 mg/l; 4 = mecoprop, 882 mg/l; 5 = 2-chlorophenol; 6 = 4-chlorophenol; 7 = 2,6-dichlorophenol; 8 = 2-methyl-4-chlorophenol; 9 = 2,4-dichlorophenol; 10 = 2,4,6-trichlorophenol; 5–10 mg/l. Eluent: methanol–0.1 *M* acetic acid (47.5:52.5) at 1.6 ml/min. UV wavelength: 280 nm. Applied potential, electrochemical detector: +1.05 V.

TABLE III

CAPACITY FACTORS, k', OF PHENOXY ACIDS AND CHLOROPHENOLS IN REVERSED-PHASE HPLC

Eluent: methanol–0.1 *M* acetic acid (47.5:52.5).

Substance	k'
2,4-D	1.2
MCPA	1.5
Dichlorprop	2.1
Mecoprop	2.5
2-Chlorophenol	0.7
4-Chlorophenol	0.9
2,6-Dichlorophenol	1.3
2-Methyl-4-chlorophenol	1.7
2,4-Dichlorophenol	2.0
2,4,6-Trichlorophenol	3.5

determination of acids and phenols in the same sample preparation is therefore preferred.

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