kieselguhr. The R_F values of 2,6-dichloro-1,4-benzoquinone, 2,3,5-trichloro-1,4-benzoquinone and chloranil obtained on silica gel layers are different and allow satisfactory identification and separation of these compounds.

Better separation of 2,6-dichloro-1,4-benzoquinone and 2,5-dichloro-1,4-benzoquinone was obtained on kieselguhr impregnated with solutions of β-phenoxyethanol in benzene, using its saturated solution in *n*-hexane as the mobile phase. The optimal separation of chlorinated *p*-benzoquinones on kieselguhr was obtained, when the concentration of β-phenoxyethanol in impregnation solution was 3.2 to 6.0 %.

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1 K. SUZUKI AND S. KATO, *Eisei Shinkenjo Kenkyu Hokoku*, 81 (1962) 51.
2 J. ELIÁŠEK AND A. JUNGWIRTH, *Collection Czech. Chem. Commun.*, 28 (1954) 2163.
3 T. SPROSTON, *Anal. Chem.*, 26 (1954) 552.
4 J. B. CONANT AND L. F. FIESER, *J. Am. Chem. Soc.*, 45 (1923) 2201.
5 A. ECKERT AND R. ENDLER, *J. Prakt. Chem.*, 104 (1922) 82.
6 S. LEVY AND G. SCHULTZ, *Ann. Chem.*, 210 (1881) 148.
7 J. GUARESCHI AND G. DACCOMO, *Chem. Ber.*, 18 (1885) 1170.
8 H. BILTZ AND W. GIESE, *Chem. Ber.*, 37 (1904) 4009.
9 A. SCHAEFFER AND D. SCHULZE, *Ger.* (*East*) *Pat.*, 12 224 (1956).

Received August 31th, 1970

CHROM 5032

A modified detection of triazine herbicide residues and their hydroxy-derivatives on thin-layer chromatograms

For the serial investigation of triazine herbicides, thin-layer chromatography (TLC) is the most suitable method at present. The detection of substances separated on the chromatogram has been tried by several methods described earlier in the literature. Among these chlorination and subsequent reaction with iodine starch proved to be the most sensitive[1]. The use of chlorine gas and some other factors, however, make the widespread application of this method difficult. Therefore, based on this reaction, a method has been developed that, besides being sensitive, might be easily and safely applied. This method is also suggested for the detection of certain triazine transformation products, hydroxy derivatives in particular.

The chlorination of triazines was performed by submersion of the layer into a carbon tetrachloride solution containing chlorine instead of chlorine gas. The potassium iodide starch solvent was substituted by a potassium iodide–*o*-tolidine solution[2] which can be stored well.

Experimental

Chlorination solution. In equal volumes carbon tetrachloride, a 3 % solution of potassium permanganate, and a 12 % solution of hydrochloric acid are carefully but vigorously mixed. The separated tetrachloride phase is filtered through a dry filter paper. In a refrigerator the solution may be stored for some days.

Detection solution. 1 g of *o*-tolidine is dissolved in 10 ml of acetic acid and 4 g of potassium iodide in distilled water, respectively. The solutions are poured together and then filled up with water to 1 l. The solution will keep well for an unlimited time.

Thin-layer. The suspension is made of 25 g of silica gel (Merck) and 60 ml of water calculated for five 20 × 20 cm layers of 250 μ thickness. The layers are activated at 120° for 30 min and then cooled to room temperature.

Development is performed in the case of triazine herbicides with a solvent mixture of toluol and acetone (85:15) (ref. 1) and in the case of hydroxy derivatives with a solvent mixture of benzene–acetic acid–water (50:50:3). The plate which has been dried at room temperature is then placed in a vessel of suitable size, into which so much chlorination solution must be poured as to cover the plate. In the case of a 18 × 24 cm vessel, 250 ml of solution are needed. Then the vessel is covered with a glass plate and from time to time shaken in order to mix the solution. (The preparation of the solution and chlorination should be carried out in a hood.)

With this amount of solution two plates can be chlorinated in succession. Chlorination takes 3 and 6 min, respectively. Then the plate is removed and dried at room temperature for about 10 min. To guarantee that the removal of chlorine gas is adequate (in the case of chlorine being present in excess the background when sprayed also turns blue, thus rendering detection of the spots impossible), it is advisable to

TABLE I

THE SENSITIVITY OF SOME DETECTION METHODS

Detection method	*Triazine herbicides ($\mu g/spot$)*			*Hydroxy derivatives ($\mu g/spot$)*		
	Prometryne	*Atrazine*	*Simazine*	*OH-propazine*	*OH-atrazine*	*OH-simazine*
Dragendorff reagent[3]	2	3	3	10	10	10
Iodine platinate[5]	1	2	2	5	5	5
Silver nitrate 0.1 *N* aq. solution[1,5]	—	0.5	0.25	—	—	—
Brilliant-Green 0.5 % acetone solution + bromine vapour[4]	2	2	3	3	3	3
Fluorescence quenching on MN UV_{254} silica gel (germicide fluorescent tube, Camag filter)[6–8]	0.2	0.4	0.4	1	1	1
Chlorination (with a chlorine-containing carbon tetrachloride solution) + *o*-tolidine–potassium iodide solution	0.02	0.05	0.05	0.1	0.2	0.2

spray the edge of the layer with the agent, and if no discolouration appears to continue spraying the whole layer. On a white background triazines are visible as blue spots. Estimation must take place within 10 min.

Results

The present method has been compared with other known detection methods. The comparison has been carried out with three triazine herbicides and their hydroxy derivatives. The results are shown in Table I.

By modification of the chlorination method of DELLEY *et al.*[1], which is no doubt the most sensitive, the following advantages were obtained. By submerging the plate in the chlorine solution, the possibility of direct contact with chlorine gas is minimal. The chlorine solution is prepared in the laboratory, so difficulties connected with the handling of chlorine gas cylinders does not occur, and health hazards are also minimized. It has to be mentioned that the chlorination solution is not suitable for spraying. According to our observations Silica Gel H does not run off from the plate during submersion. By reaction with potassium iodide–*o*-tolidine subsequent to chlorination, we obtained the greatest possible sensitivity which can be generally obtained with a starch-containing agent. Subsequent to chlorination the detection with potassium iodide–*o*-tolidine can be combined with the informative fluorescence quenching method because the chlorination of triazines can also be carried out on MN UV_{254} silica gel.

Thanks are due to Mrs. IRENE LEDER for her technical assistance.

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1 R. DELLEY, K. FRIEDRICH, B. KARLHUBER, G. SZÉKELY AND K. STAMMBACH, *Z. Anal. Chem.*, 228 (1967) 23.
2 K. MACEK AND J. VECERKOVA, *Pharmazie*, 20 (1965) 605.
3 H. G. HENKEL AND W. EBING, *J. Chromatog.*, 14 (1964) 283.
4 D. C. ABBOTT, S. A. BUNTING AND S. THOMSON, *Analyst*, 90 (1965) 35.
5 K. STAMMBACH, H. KILCHHER, K. FRIEDRICH, M. LARSEN AND G. SZÉKELY, *Weed Res.*, 4 (1964) 64.
6 R. W. FREI, N. S. NOMURA AND M. N. FRODYMA, *Mikrochim. Acta*, 6 (1967) 1099.
7 L. P. MANNER, *J. Chromatog.*, 21 (1966) 430.
8 S. KOUDELA, *Kisérl. Orvostudományy*, 19 (1967) 331.

First received May 22nd, 1969; revised manuscript received August 25th, 1970