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## Note

# Determination of ametrine and atrazine residues in soil by thin-layer chromatography

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The increasing use of triazine herbicides in weed control necessitates that degradation rate and residue levels in different environments be determined. The analytical procedures mostly used are based on thin-layer chromatography (TLC)[1–7] and gas–liquid chromatography (GLC)[8,9].

In our work, it was necessary to determine the degradation rates of the triazine herbicides atrazine (2-chloro-4-ethylamino-6-isopropylamino-*s*-triazine) and ametrine (2-methylmercapto-4-ethylamino-6-isopropylamino-*s*-triazine) in soil, and the following analytical procedure was used.

## EXPERIMENTAL

### *Extraction*

A portion of about 1 kg was taken from a field sample of soil, air-dried and ground to about 20 mesh. An amount of 20 g of soil sample was weighed into a 100-ml erlenmeyer flask fitted with a stopper. A 1-ml volume of ammonia solution (25%) was added, and the mixture was vigorously shaken on a mechanical shaker with three 50-ml portions of diethyl ether. The combined extracts were filtered through anhydrous sodium sulphate, and the volume was reduced to 10–15 ml on a rotary evaporator, transferred to a 25-ml calibrated flask and made up to the mark with diethyl ether. A suitable aliquot was transferred to a 25-ml tube with a narrow conical bottom and evaporated to dryness by means of a moderate dry air current, and the remaining residue was dissolved in a few drops of chloroform.

### *Clean-up*

The dissolved residue was quantitatively applied as one spot (diameter 0.5 cm) to the starting line of a chromatoplate covered with a thin layer of Alumina G, to which 0.01 % of Uranin A (BASF) fluorescent colour had been added. Near this spot, at a distance of about 2.5 cm, a mixture of standard (0.5–2.0 $\mu$g) ametrine and atrazine solution was applied. After separation by the ascending technique with a carbon disulphide–ethyl acetate mixture (8:1), the plate was dried with a hair-drier and the spots were observed under UV light (Uvis, Desaga lamp) at 254 nm and marked with

a pencil. The marked layer was scraped off and eluted with 3–4 ml of a 2% solution of methanol in chloroform into tubes with narrow conical bottoms and evaporated.

*Determination*

After rinsing the walls of the tube with several drops of chloroform, the contents were carefully evaporated to a volume of about 50 $\mu$l and quantitatively transferred to a Silica Gel $G_{254}$ (Merck) chromatoplate. The chromatoplate was developed in a carbon disulphide–ethyl acetate mixture (8:2), removed from the tank, dried and observed under UV light at 254 nm, comparing the area of the spot of the unknown compound with those of standards carried through the same procedure.

## RESULTS AND DISCUSSION

In our investigations in 1969–1971 (Project IIIa/2), we studied the degradation rate of two triazine preparations: atromet (a suspension of 34% atrazine and 16% ametrine mixture, "Radonja", Sisak, Yugoslavia) and atrazine (a suspension of 50% atrazine, "Radonja", Sisak, Yugoslavia). The preparations were applied to different types of soil at concentrations of 1 and 2 kg/ha, and the degradation was determined at intervals of 4 months during a 2-year period. The extraction and determination of triazine were carried out immediately after drying the soil in the laboratory.

In previous investigations on untreated samples of soil, various analytical procedures were tested, but none was satisfactory. Abott *et al.*[1] applied a relatively simple procedure for the removal of acidic and neutral co-extractives by extraction with diethyl ether from a 0.1 *N* solution of hydrochloric acid, whereupon a 72% recovery of atrazine was obtained. Frei and Duffy[2] obtained an 82% recovery of ametrine by using a radiochemical method of detection. Our attempts to use these techniques (Table I) showed that it is possible to obtain 80–83% recovery of ametrine and only 17–20% of atrazine. Further investigations indicated that 80% of atrazine is lost with the discarded ether after extraction from acidic medium.

TABLE I

RECOVERY OF AMETRINE AND ATRAZINE FROM SOIL

| *Triazine* | *Added (μg per 20 g)* | *Abott et al.*[1] | | *This work* | |
|---|---|---|---|---|---|
| | | *Found (μg per 20 g)* | *Recovery (%)* | *Found (μg per 20 g)* | *Recovery (%)* |
| Ametrine | 1 | 0.8 | 80 | 0.8 | 80 |
| | 3 | 2.5 | 83 | 2.5 | 83 |
| | 5 | 4.0 | 80 | 4.0 | 80 |
| Atrazine | 1 | — | — | 1.0 | 100 |
| | 3 | 0.5 | 17 | 3.0 | 100 |
| | 5 | 1.0 | 20 | 5.0 | 100 |

For these reasons necessary modifications in cleaning up the crude extract were made by using TLC on alumina to which Uranin A had been added. By using the solvent carbon disulphide–ethyl acetate (8:1), we were able to localize the coextractives below the solvent front, leaving the middle of the chromatogram relatively

clear. The spots of triazine were sufficiently separated to be scraped off and further eluted for the purpose of re-chromatography and the determination of the residue content. Re-chromatography was performed on a thin layer of Silica Gel $G_{254}$ with carbon disulphide–ethyl acetate (8:2)[3], whereupon $R_F$ values of 0.46 for atrazine and 0.54 for ametrine were obtained.

The spots of the triazines were symmetrical in shape, and their area was proportional to the concentration[1] within limits between 0.5 and 2.0 $\mu$g. The recovery of ametrine was 80% and of atrazine 100%.

Fluorescence quenching[3,4] in order to make the spots on the chromatogram visible represents a considerable improvement in relation to coloured reactions because of its non-destructive nature and its capacity to decrease the level of detection. The procedure described makes possible the detection of amounts as low as about 0.1 $\mu$g per spot of triazine (about 0.005 p.p.m.), which would be especially useful in the control of river and lake waters near Beograd. The presence of organochlorine insecticides does not interfere in the detection of triazines, but some interferences are possible with regard to the non-specific procedure of detection. In such instances, some of the suitable procedures available[6,7] could be used to continue investigations.

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