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Note

Determination of 1,3,5-triazine herbicides by gas chromatography¹

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Derivatives of 1,3,5-triazine (*sym.*-triazine) with pronounced herbicidal properties are an important chemical means of plant protection. The herbicidal efficiency of *sym.*-triazines depends on the substituent in position 2 ($-\text{Cl}$, $-\text{OCH}_3$ or $-\text{SCH}_3$) and on the total number of carbon atoms in the aminoalkyl groups in positions 4 and 6; a change in the substituent in position 2 also causes a change in the selective effect of the compound. More pronounced herbicidal effects have been obtained by applying triazines in combination (*e.g.*, terbutylazine and terbutone in Caragard Combi A50 WP (see Table I), possibly in mixtures with other chemicals.

Low doses of triazine herbicides affect the roots of plants; higher doses may have stimulating effects and may cause soil sterility. Hence, the use of these herbicides may cause undesirable effects. Substances that enhance the production of agricultural plants adversely affect the environment by leaving undesirable residues, which may exert pathogenic (and sometimes also mutagenic) effects on living organisms.

sym.-Triazine derivatives have been determined by spectrophotometry in the visible and UV regions, by paper chromatography and by thin-layer chromatography¹⁻³. These methods have certain limitations; paper chromatography and TLC are unsuitable for quantitative analysis, and spectrophotometry fails with multi-component mixtures. Thus, gas chromatography (GC) is now used almost exclusively⁴⁻²⁰. The results of a previous study of the behaviour of *sym.*-triazine derivatives¹⁴ were used in this work when determining the active components of the triazine herbicides in sprays and in soil.

EXPERIMENTAL

Materials

Standard *sym.*-triazines (atrazine, simazine, methoprotrolyne, terbutryne, terbutylazine, prometryne, desmetryne, terbutone) were obtained from Ciba-Geigy (Basel, Switzerland); all the herbicides except Zeazin 50 (CHZJD, Czechoslovakia) were also products of Ciba-Geigy.

Methanol, p.a. (Lachema, Brno, Czechoslovakia), was redistilled before use. Chloroform, p.a., and the Chromaton N/AW support (60-80 mesh) were also obtained from Lachema; the SE-30 phase was from Carlo Erba (Milan, Italy) and the Reoplex 400 from Varian AG (Zug, Switzerland).

Spectrophotometry

Spectrophotometric measurements were performed on methanolic solutions at 225 nm with a Specord UV-VIS instrument (Zeiss, Jena, G.D.R.) and 0.5-cm quartz cells. An atrazine standard solution (50 μM) was prepared in methanol, and a calibration curve was constructed for atrazine over the concentration range 5 to 50 μM . Then a solution of Semparol in methanol was prepared, which was *ca.* 10 μM in atrazine. By referring its absorbance to the calibration curve, the atrazine concentration in Semparol (namely, 29.2%) was determined.

Gas chromatography

The measurements were carried out on a Hewlett-Packard 5700A instrument equipped with flame ionization detection. The stainless-steel column (144 cm \times 3 mm I.D.) was packed with a mixture of 2% of Reoplex 400 and 5% of SE-30 supported on Chromaton and was operated at 195°, with a carrier gas (nitrogen) flow-rate of 40 ml/min, an injector temperature of 220° and a detector temperature of 195°.

Determination of *sym.*-triazines in herbicide preparations

Pure standard *sym.*-triazines were available so that absolute calibration with direct comparison was used. Chloroform solutions (*ca.* 1 $\mu\text{g}/\text{ml}$) of the preparations were used, 1- μl portions of these solutions being injected into the gas chromatograph; the areas of the corresponding peaks (A_i) were found. Then 1 μl of the triazine standard solution was injected under identical conditions, and the peak area (A_s) was measured. The percentage concentration (c_i) of the active component of the herbicide was calculated from the relationship

$$c_i = \frac{A_i}{A_s} \cdot \frac{m_s}{m_i} \cdot 100$$

where m_i is the amount of herbicide in 1 μl of solution and m_s that of *sym.*-triazine in 1 μl of standard solution. Each measurement was carried out five times.

Determination of atrazine in soil

An experimental area (1 m² in size) was sprayed with a solution containing 1 g of Semparol in 600 ml of water. Composite soil samples taken after 8, 15 and 23 days were dried to constant weight in air at room temperature. Then 100 g of dry soil were extracted with acetonitrile-water (9:1), and the extract was purified on column of alumina (Woelm; activity V) recommended by Mattson *et al.*¹⁵. The amount of atrazine in the extract was determined by the absolute calibration method. A standard solution containing 0.5 μg of atrazine in 1 μl of chloroform was prepared; and a calibration curve was established by injecting 0.4 to 1.6 μl of this solution into the chromatograph. Then 2 μl of the soil extract were injected, and the atrazine concentration was read from the graph.

RESULTS AND DISCUSSION

The results of the determination of active components in *sym.*-triazine herbicides are given in Table I, the precision of the determination being shown by standard

deviation (*s*). Some of the higher values of *s* can be attributed to inhomogeneity of the preparation. It can be seen that GLC is a precise and rapid method for analysing multi-component *sym.*-triazine herbicides.

TABLE I
DETERMINATION OF *sym.*-TRIAZINES IN TECHNICAL PRODUCTS

<i>Herbicide</i>	<i>Triazine</i>	<i>Content stated by manufacturer (%)</i>	<i>Content found by GC (%)</i>	<i>Standard deviation (s)</i>
Semparol 1167	Atrazine	30	28.8	1.2
Zeazin 50	Atrazine	50	50.9	2.1
Gesaprim 50	Atrazine	50	51.5	2.5
Gesatop 50	Simazine	50	50.0	0.5
Gesaran 2079	Simazine	5	6.3	0.2
	Methoprotryne	22.5	30.6	1.2
Agren 3614	Simazine	4	3.6	0.3
	Terbutryne	18	20.7	1.0
Igran 50	Terbutryne	50	48.5	0.6
Topograd 3623	Terbutryne	35	34.9	1.1
	Terbutylazine	15	14.5	0.8
Gesagard 50	Prometryne	50	52.6	2.0
Semeron 25WP	Desmetryne	25	24.8	0.3
Etazin 50	<i>sec.</i> -Bumetone	50	45.4	2.1
Caragard Combi A50WP	Terbutylazine	25	24.1	0.4
	Terbutone	25	22.5	0.5

The GC method was compared with the spectrophotometric procedure on samples of Semparol. The spectrophotometric value (29.2%) was in good agreement with the results of GC. The spectrophotometric method is highly sensitive, but its application is limited. Because the absorption spectra of *sym.*-triazines are similar^{14,16}, such spectra cannot be used for differentiating between individual triazines, but can only be applied to herbicides containing a single triazine and no other substances that absorb at 225 nm. These conditions were met with Semparol, so that comparison of the methods was possible.

Because of the low triazine concentration in soil, the soil extract must be purified on a column before GC. Even then, the extract contains a number of substances as well as atrazine (Fig. 1a), and these may interfere in determination of the atrazine. For this reason, a blank determination on a sample of atrazine-free soil was carried out in parallel (Fig. 1b). As the atrazine concentration in soil was rather high (of the order of a few ppm), the flame ionization detector could be used to advantage. The least detectable amount (*ca.* 4 ng) indicates that this detector could be used even for the determination of very low concentrations (tens of ppb), provided that the amounts of other substances in the extract were low. Otherwise, specific detectors must be used^{5,7,9-11,13,19,20}.

The atrazine concentration in soil decreases exponentially with time (Fig. 2). Triazines are decomposed by light, evaporate owing to their volatility, are adsorbed on soil and are degraded by micro-organisms or by hydrolysis and oxidation. It is difficult to evaluate the effect of each individual factor on the fate of triazines in soil,

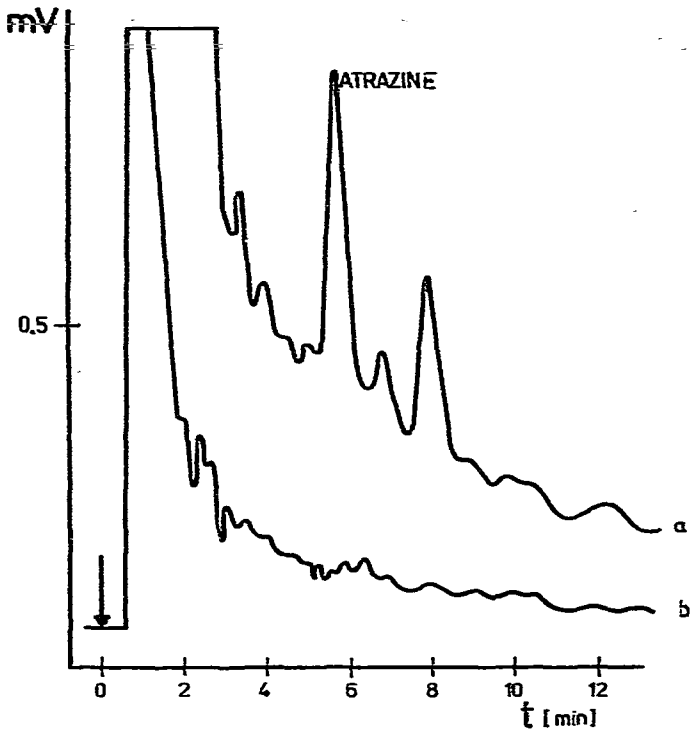


Fig. 1. Gas chromatograms of (a) soil extract containing atrazine and (b) blank. For experimental conditions see text.

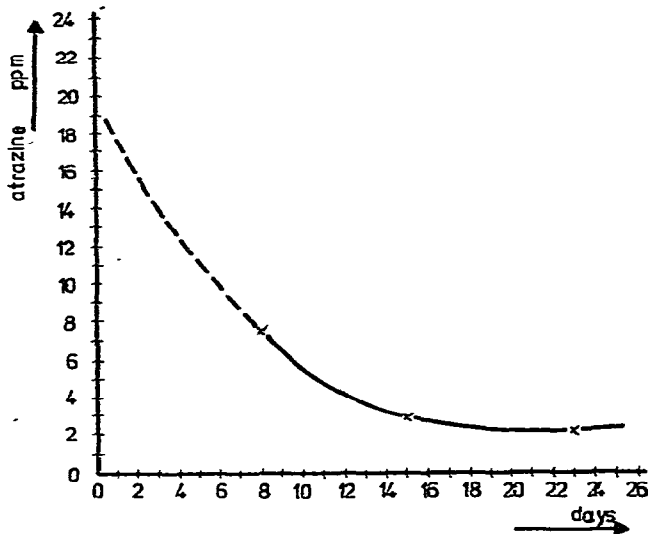


Fig. 2. Decay of strazine in soil.

as they vary with such climatic parameters as temperature and amount of precipitation. For these reasons, this work is not intended to be a biological study, but only to demonstrate the usefulness of GC with flame ionization detection for the determination of *sym.*-triazines in soil.

REFERENCES

- 1 R. Delley, K. Friedrich, B. Karlhuber, G. Szekely and K. Stambach, *Z. Anal. Chem.*, 228 (1967) 23.
- 2 E. Knüsl, H. P. Burchfield and E. E. Storrs, in G. Zewig (Editor), *Analytical Methods for Pesticides, Plant Growth Regulators and Food Additives*, Vol. IV, Academic Press, New York, 1964.
- 3 J. A. Guth and L. P. Manner, *J. Chromatogr.*, 30 (1967) 514.
- 4 K. Stambach, H. Kilchner, M. Larsen and G. Szekely, *Weed Res.* 4 (1964) 64.
- 5 D. E. Otto, *J. Ass. Offic. Anal. Chem.*, 54 (1971) 1388.
- 6 K. Ramsteiner, W. D. Hörmann and D. O. Eberle, *J. Ass. Offic. Anal. Chem.*, 57 (1974) 192.
- 7 W. D. Hörmann, G. Formica, K. Ramsteiner and D. O. Eberle, *J. Ass. Offic. Anal. Chem.*, 55 (1972) 1031.
- 8 C. J. Harris, *Weed Res.*, 5 (1965) 275.
- 9 H. J. Young and A. Chu, *J. Agr. Food Chem.*, 21 (1973) 711.
- 10 W. E. Westlake, A. Westlake and F. A. Gunther, *J. Agr. Food Chem.*, 18 (1970) 686.
- 11 J. F. Lawrence, *J. Agr. Food Chem.*, 22 (1974) 137.
- 12 M. A. Berezovsku and G. N. Nemova, *Agrokimiya*, 1973, 12.
- 13 M. C. Bowman and M. Beroza, *J. Ass. Offic. Anal. Chem.*, 53 (1970) 499.
- 14 V. Pacáková and I. Němec, *J. Chromatogr.*, 148 (1978) 273.
- 15 A. M. Mattson, R. A. Kahrs and R. T. Murphy, *The Triazine Herbicides, Residue Reviews*, Vol. 32., Springer Verlag, Berlin, 1970, p. 371.
- 16 H. Kozáková, Thesis, Charles University, Prague, 1976.
- 17 E. D. Chilwell and D. Hughes, *J. Sci. Food Agr.*, 13 (1962) 425.
- 18 C. A. Benfield and E. D. Chilwell, *Analyst (London)*, 89 (1964) 475.
- 19 W. P. Cochrane, B. P. Wilson and R. Greenhalgh, *J. Chromatogr.*, 75 (1973) 207.
- 20 R. Greenhalgh and W. P. Cochrane, *J. Chromatogr.*, 70 (1972) 37.