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Application of a Thermionic Detector in the Analysis of *s*-Triazine Herbicides

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The response characteristics and retention times of seven *s*-triazine herbicides have been studied using a thermionic detector fitted with a cesium bromide (CsBr) tip and various gas chromatographic columns such as OV-17, SE-30, Reoplex-400, and Carbowax 20M. Thermionic detection using the Carbowax 20M column gave sensitivities comparable to those by Coulson electrolytic conductivity detector. Recoveries of atrazine added to water at 0.02, 0.05, and 2.0 ppm were between 92 and 122%; for corn at 0.1, 0.2, and 1.0 ppm, between 101 and 110%; and for soil at 0.23, 0.46, and 1.1 ppm, between 88 and 101%. The detector has also been applied to an evaluation of some extraction procedures and extracting solvents for atrazine residue in a field treated soil.

A variety of *s*-triazine herbicides are used for weed control in crops and methods are needed for their selective detection and determination at the residue level. Since the *s*-triazines contain nitrogen in their molecular structure, detectors responding to nitrogen would be most useful for their residue analysis. The recent availability of thermionic detectors has prompted some workers to investigate their utility for the residue analyses of *s*-triazines (Ebing, 1968; Tindle *et al.*, 1968; Schultz, 1970; McKone *et al.*, 1972). Tindle *et al.* (1968) used a $RbSO_4$ thermionic detector for the determination of atrazine, simazine, propazine, and prometryne residues in water, soil, and corn. They reported minimum detectable limits better than 0.5 ng of *s*-triazine, with a very favorable selectivity of response for organo-nitrogen compounds compared to carbonaceous materials. Schultz (1970) used a CsBr phosphorus detector for the determination of some *s*-triazine herbicides in crops. The minimal detectable amounts based on 3% full scale deflection were about 0.5 ng of atrazine and 1.0 ng of Bladex (SD15418).

The aim of the present work was to investigate the gas chromatographic characteristics of *s*-triazines using a thermionic detector with a CsBr tip. Since atrazine is the most widely used herbicide among the *s*-triazines, the use of a thermionic detector for the residue analysis of this herbicide in water, soil, and corn samples was also investigated.

EXPERIMENTAL SECTION

Chemicals. All solvents were of pesticide grade and used as received. Atrazine [2-chloro-4-(ethylamino)-6-(isopropylamino)-*s*-triazine], atratone [2-(ethylamino)-4-(isopropylamino)-6-methoxy-*s*-triazine], ametryne [2-(ethylamino)-4-(isopropylamino)-6-(methylthio)-*s*-triazine], prometone [2,4-bis(isopropylamino)-6-methoxy-*s*-triazine], prometryne [2,4-bis(isopropylamino)-6-(methylthio)-*s*-triazine], propazine [2-chloro-4,6-bis(isopropylamino)-*s*-triazine], and simazine [2-chloro-4,6-bis(ethylamino)-*s*-triazine] were analytical reference grade samples obtained from CIBA-Geigy. Solutions of these herbicides were prepared in methanol.

Determination of Residues in Water, Soil, and Corn Samples Fortified with Atrazine. (a) *Water.* The water samples (100–500 ml) were fortified with a standard solution of atrazine in methanol at the 0.02-, 0.05-, and 2.0-ppm levels. The fortified sample was transferred to a separatory funnel and extracted with three 70-ml portions of methylene chloride. The extracts were combined, dried with anhydrous Na_2SO_4, and concentrated to a small volume by rotary vacuum evaporation at about 35°. The material was quantitatively transferred on the top of a deactivated (13% H_2O) alumina column (0.8 in. diameter, 25 g of aluminum oxide W200 basic, Woelm, previously washed with 100 ml of CCl_4) topped with 0.5 in. of anhydrous Na_2SO_4. The column was eluted with 100 ml of 2% diethyl ether in carbon tetrachloride. No atrazine was eluted by this eluate. Following this the column was eluted with 200 ml of 6% diethyl ether in carbon tetrachloride and the collected eluent was evaporated to dryness in a rotary evaporator. The residue was dissolved in hexane and analyzed by gas chromatography.

(b) *Corn.* The corn samples were chopped and finely ground. Subsamples (5 g) were fortified with atrazine in methanol at the 0.1-, 0.2-, and 1.0-ppm levels. The fortified sample was extracted with acetonitrile (100 ml) with mechanical shaking for 90 min. The mixture was filtered under suction through a Hyflo Super-Cel bed and the filter bed was washed with 100 ml of 35% aqueous acetonitrile. The combined filtrate was partitioned with hexane and the aqueous phase was collected. The hexane phase was repartitioned with aqueous acetonitrile. The combined aqueous phase was extracted with three 50-ml por-

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tions of methylene chloride. The extracts were combined, dried with anhydrous Na_2SO_4, concentrated in a rotary evaporator, and cleaned up by chromatography on a deactivated alumina column as described before. The collected eluent was evaporated to dryness in a rotary evaporator and the residue dissolved in hexane and analyzed by gas chromatography.

(c) *Soil.* The soil (Granby sandy loam, organic matter 8.8%) was obtained in bulk (6 in. depth) from an area which had not been previously treated with *s*-triazine herbicides. The soil was air dried at room temperature, pulverized, screened through a 20-mesh screen, and mixed thoroughly by tumbling. Subsamples (20 g) were fortified with atrazine in methanol at the 0.23-, 0.46-, and 1.1-ppm levels. The fortified sample was extracted with 50 ml of acetone in a Goldfisch extractor (Fisher Scientific Co.) for 24 hr. The extract was evaporated to dryness in a rotary evaporator and the residue dissolved in hexane and analyzed by gas chromatography.

Determination of Atrazine Residue in Soil Collected from the Field. Soil samples (Grenville sandy loam, organic matter 2.4%) were obtained from the corn growing experimental plots with a known history of atrazine treatment. Twenty-four 6-in. deep soil cores were taken from the treated or the adjacent check plots, air dried at room temperature, pulverized, screened through a 20-mesh screen, and mixed thoroughly by tumbling. The atrazine residues were extracted from the subsamples by the following methods.

(1) *Mechanical Shaker.* Thirty grams of soil was shaken with 100 ml of acetone on a mechanical shaker for 1 and 24 hr. The mixture was filtered under suction through a Hyflo Super-Cel bed and the filter bed was washed with three 50-ml portions of acetone. The filtrate and washings were combined and evaporated to dryness in a rotary evaporator. The residue was dissolved in 35% aqueous acetonitrile and extracted with methylene chloride (100 ml × 2). The methylene chloride extract was dried with anhydrous Na_2SO_4 and evaporated to dryness in a rotary evaporator.

(2) *Soxhlet.* Thirty grams of soil was extracted with 100 ml of acetone in a Soxhlet extractor for 1 and 24 hr. Acetone was removed by rotary vacuum evaporation. The residue was dissolved in 35% aqueous acetonitrile and further processing was done as described in method 1.

(3) *Goldfisch.* Thirty grams of soil was extracted with 50 ml of acetone in a Goldfisch extractor for 1 and 24 hr. Acetone was removed by rotary vacuum evaporation and residue dissolved in 35% aqueous acetonitrile solution. Further processing of the extract was done as described in method 1.

(4) *Refluxing.* Thirty grams of soil was heated under reflux with 100 ml of acetone in a boiling flask for 1 and 24 hr. The mixture was filtered and the extract was processed as described in method 1.

Column Cleanup. The dried materials obtained by methods 1–4 were dissolved in small volumes of carbon tetrachloride, cleaned up by chromatography on a deactivated alumina column as described before, and finally analyzed by gas chromatography.

All samples were analyzed in duplicate and average values are reported. The results were corrected for the interference levels observed in the blank samples. Residues in soils are reported on an oven dry basis.

Gas Chromatography. The gas chromatograph was a Pye series 104, Model 124 fitted with a thermionic detector having a CsBr Annulus. Columns were: 5 ft × 0.25 in. o.d. glass tubes packed with 5% Reoplex 400 or 3% Carbowax 20M; 3 ft × 0.25 in. o.d. glass tube packed with 3% OV-17; and 5 ft × 0.25 in. o.d. stainless steel tube packed with 3% SE-30. All liquid phases were coated on 80–100 mesh Chromosorb W-HP. The operating conditions were: column temperature, in the range of 219–243° as indicated; detector and injector temperatures, 190 and 150°, respectively; nitrogen carrier flow, 40 ml/min; hydrogen flow, 40 ml/min; and air flow, 420 ml/min. Peak height was used for quantitation.

RESULTS AND DISCUSSION

The comparative response of the various *s*-triazines on four different columns using the thermionic detector is shown in Table I. The 3% Carbowax column appears to separate most of the compounds with good resolution. The other three columns did not give adequate separation for all the herbicides examined. Under the gc conditions described, the response of the various *s*-triazines (concentration range used 1–20 ng) was linear and the compounds gave a 50% full scale deflection (½ fsd) in the 4–15-ng range. For most of the *s*-triazines higher sensitivities were obtained with the 3% OV-17 and 3% Carbowax 20M columns in comparison to the 3% SE-30 and 5% Reoplex 400 columns. Although the OV-17 column gave sensitivities comparable to those of the Carbowax 20M column, the former gave poor resolution of the compounds (Table I). Purkayastha and Cochrane (1973) obtained higher sensitivities with the 3% Carbowax 20M column in comparison to 5% Reoplex 400 column for *s*-triazine herbicides. They noted that for most of the *s*-triazines a sample weight in the 10–30-ng range was required for ½ fsd using a Coulson electrolytic conductivity detector. Cochrane and Wilson (1971) used 3% OV-1 and 5% OV-17 columns and observed that some of the *s*-triazines gave a ½ fsd in the range of 7–15 ng using a Coulson electrolytic conductivity detector. The data obtained in this study (Table I) and those reported by other workers (Schultz, 1970; Cochrane and Wilson, 1971; Purkayastha and Cochrane,

Table I. Retention Times and Thermionic Detector Response of *s*-Triazine Herbicides

	3% SE-30 (219°)		5% Reoplex 400 (229°)		3% OV-17 (219°)		3% Carbowax 20M (243°)	
Herbicide	R_t, min	1/2 fsd,[a] ng	R_t, min	1/2 fsd, ng	R_t, min	1/2 fsd, ng	R_t, min	1/2 fsd, ng
Prometone	2.1	11.4	0.9	7.1	0.5	4.9	1.5	4.3
Atratone	2.1	13.4	1.2	8.1	0.6	4.7	1.9	4.3
Propazine	2.2	8.6	1.3	7.5	0.6	4.2	2.5	4.8
Atrazine	2.3	10.0	1.7	10.1	0.6	5.0	2.7	6.6
Simazine	2.5	10.8	2.0	13.1	0.6	4.8	3.9	8.6
Prometryne	3.6	14.3	1.6	10.6	0.9	8.0	2.9	7.5
Ametryne	3.9	15.7	2.0	10.4	1.0	7.6	3.6	8.9

[a] 50% full scale deflection.

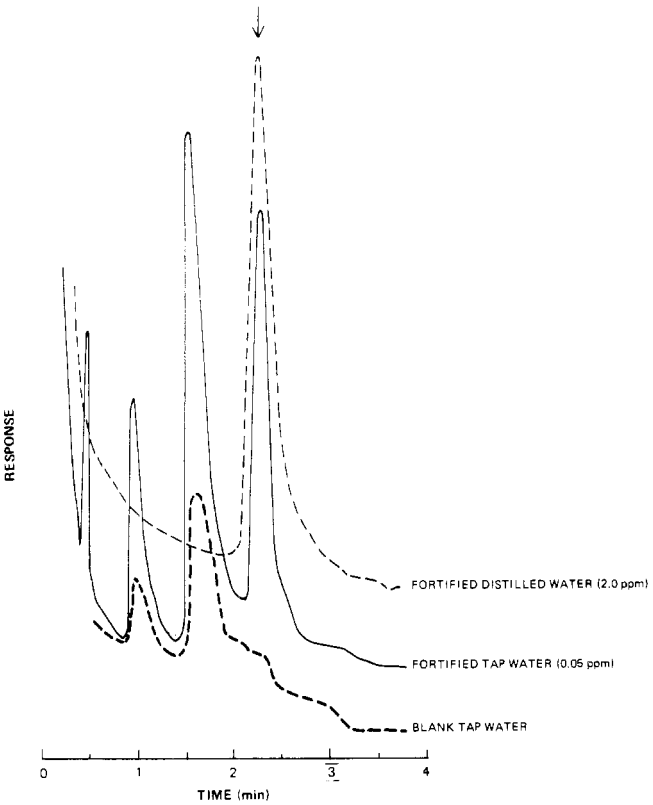

Figure 1. Gas chromatograms from determination of atrazine in fortified water. Gc conditions: stainless steel column 5 ft × 0.25 in. o.d. packed with 3% SE-30 on Chromosorb W-HP; column temperature, 219°; detector and injector temperatures, 190 and 150°, respectively; nitrogen carrier flow, 40 ml/min; hydrogen flow, 40 ml/min; and air flow, 420 ml/min.

Table II. Recovery of Atrazine from Fortified Water, Corn, and Soil

Material	Atrazine, ppm Added	Recovered	% recovery
Water[a]	0.02	0.024	121.5
	0.05	0.046	92.5
	2.00	2.006	100.3
Corn[b]	0.10	0.106	106.0
	0.20	0.202	101.0
	1.00	1.098	109.8
Soil[c]	0.23	0.202	88.0
	0.46	0.465	101.0
	1.10	0.963	87.5

[a] Dichloromethane extraction. [b] Acetonitrile extraction. [c] Goldfisch extraction with acetone.

1973; Young and Chu, 1973; Lawrence, 1974) suggest that the thermionic and Coulson electrolytic conductivity detectors have nearly similar sensitivities for s-triazine herbicides.

Figure 1 shows the gas chromatographic tracings of the blank and fortified water samples. A few unknown peaks appeared in the chromatograms due to coextractives but they did not interfere with the herbicide peak. Recoveries of atrazine from the fortified water samples ranged from 92.5 to 121.5% (Table II). At 0.05- and 2.0-ppm levels the recovery was fairly good and in all cases a good detectable chromatographic peak for atrazine was obtained. At the

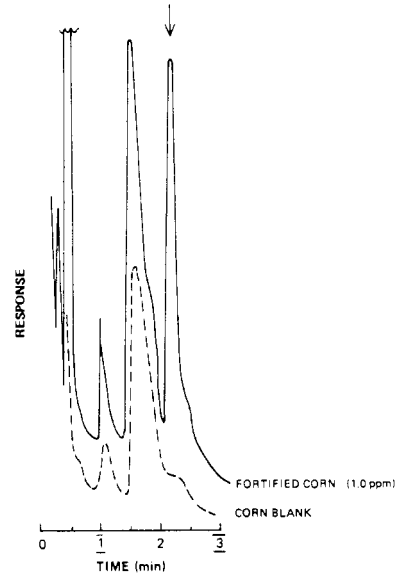

Figure 2. Gas chromatograms from determination of atrazine in fortified corn. Gc conditions same as in Figure 1.

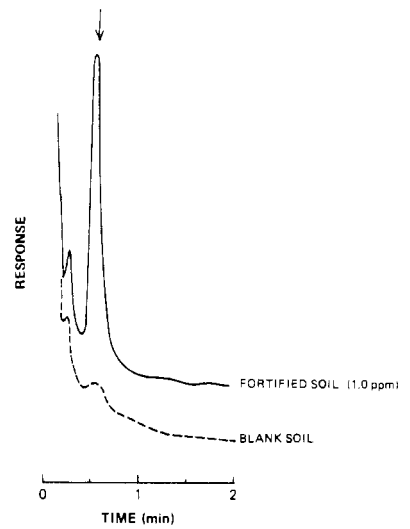

Figure 3. Gas chromatograms from determination of atrazine in fortified soil. Gc conditions same as in Figure 1 except 3% OV-17 column.

0.2-ppm level the recovery was high indicating interference at this level by coextractives.

Typical gas chromatograms of corn samples obtained with the thermionic detector are shown in Figure 2. The background interference for the corn sample at 0.1-, 0.2-, and 1.0-ppm fortification levels was 32.0, 17.0, and 7.2 ppb, respectively. However, at these fortification levels satisfactory recoveries were obtained by thermionic detector after the usual cleanup (Table II).

The blank soil chromatogram showed a background interfering peak at the appropriate retention time of atrazine (Figure 3). In general, the recovery of atrazine was fairly good from soil samples fortified with atrazine (Table II). While this is not a true indication of extraction efficiency as applied to field treated soil, it does show that little loss of atrazine was experienced during extraction.

The method has been used to determine the atrazine residue in a field treated soil. Table III shows the results obtained with four different extraction methods. Heating under reflux and Goldfisch methods were more efficient than the other two methods. Increase in time of extraction

Table III. Effect of Extraction Method and Time of Extraction on the Recovery of Atrazine Residue from the Field-Treated Soil[a]

Description of extraction method	Recovy of atrazine residue, ppb	
	1 hr	24 hr
Mechanical shaker	74	138
Reflux	149	163
Soxhlet	102	142
Goldfisch	126	166

[a] Acetone extraction.

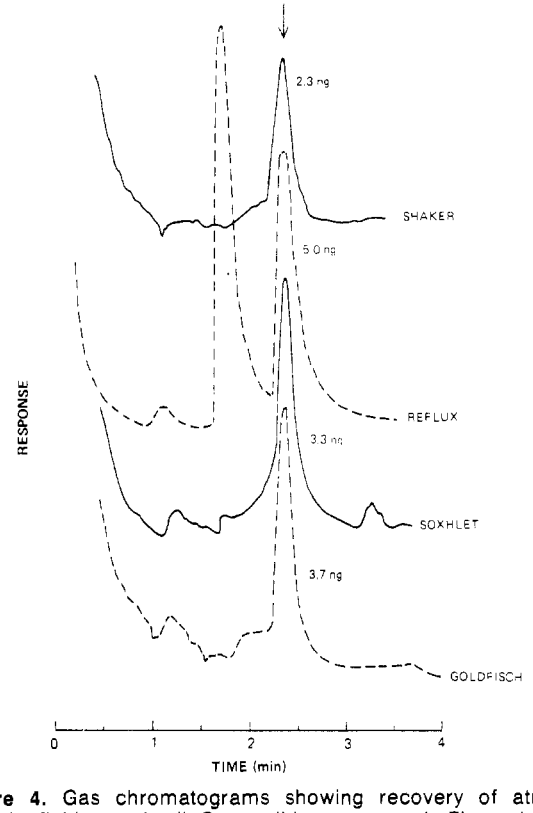

Figure 4. Gas chromatograms showing recovery of atrazine from the field-teated soil. Gc conditions same as in Figure 1.

from 1 to 24 hr resulted in an improved recovery of atrazine residue. At a given time mechanical shaker and Soxhlet extractions resulted in poor recoveries. Figure 4 compares gas chromatograms obtained by the different methods using acetone as the extracting solvent and utilizing column cleanup. An unknown major peak (R_t = 1.8 min, Figure 4) always appeared in the chromatograms of the field-treated and blank soil samples extracts obtained by heating under reflux but it did not interfere with the atrazine peak.

The relative extraction efficiency of various solvents is compared in Table IV. The soil was heated with the solvent under reflux for 1 hr. Acetone gave a higher recovery of atrazine residue from the field-treated soil than any other solvent. Hexane gave very poor recovery while most of the other solvents showed intermediate values. The variations in the extraction efficiencies of these solvents were not related to the solubility of atrazine in these solvents. Atrazine is more soluble in chloroform than methanol but the latter extracted more atrazine from the soil than the former. In general, more polar solvents were less coextractive than the polar solvents. There was no connection between the amount of atrazine found and the amount of coextractives. Methylene chloride was preferred over the other partitioning solvents because of the fewer impurities extracted.

Table IV. Effect of Solvent on the Recovery of Atrazine Residue from the Field-Treated Soil[a]

Solvent	Recovy of atrazine residue, ppb
Dichloromethane	58.5
Hexane	4.6
Carbon tetrachloride	61.8
Chloroform	33.8
Methanol	68.0
Acetonitrile	66.0
90% (v/v) methanol–water	73.0
90% (v/v) acetonitrile–water	67.0
Acetone	149.0

[a] Heating under reflux for 1 hr.

CONCLUSIONS

This study has shown that after extraction and cleanup, atrazine residues can be determined in water, soil, and corn samples by gas chromatography using a nitrogen-selective thermionic detector fitted with a CsBr tip. The residue methods developed for atrazine may be applicable, with some modification, to other *s*-triazines. The sensitivity and capability of the thermionic detector are comparable to the Coulson electrolytic conductivity detector previously employed for the analyses of *s*-triazines (Cochrane and Wilson, 1971; Purkayastha and Cochrane, 1973; Lawrence, 1974). Heating under reflux or Goldfisch extraction with solvent, such as acetone, appears to be an effective method for recovering atrazine residue from the field-treated soil.

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