Microdetermination of Chloro-s-triazines in Soil by Gas–Liquid Chromatography with Nickel Electron Capture or Electrolytic Conductivity Detection

Hong Y. Young* and Ada Chu

The Cl-s-triazines simazine, atrazine, and propazine are extracted from soil with a mixture of ethyl acetate and methanol and determined by gas–liquid chromatography with nickel electron capture or electrolytic conductivity detection. Cleanup is necessary for the former but not the latter detector. Sensitivity is placed at 1 ng in the injected sample and the least determinable concentration at 0.1 ppm of soil. Recovery of added triazine ranged from 84 to 112%.

The chloro-s-triazines simazine, atrazine, and propazine have been found to be effective herbicides in agriculture. In Hawaii atrazine, in particular, is being used in sugarcane culture and, in special situations, in pineapple culture.

The determination of triazine herbicides in soil has been reviewed by Mattson *et al.* (1970) and a coulometric method has been described having a sensitivity of approximately 25 ng for atrazine in the injected sample. Tritium electron capture (EC) detection was considered to be relatively insensitive, as 100–300 ng were required for a half full-scale deflection (FSD). Similar values have been reported by Burke and Holswade (1966). Cochrane and Wilson (1971) have reported much higher sensitivity values of 1.1–2.2 ng for half-FSD with the nickel EC detector and 7 ng by the conductivity detector using standard solutions.

This report describes a method applied to the determination of chloro-s-triazine residues in soil using a nickel EC detector which is capable of giving half FSD at 10–15 ng levels and detecting 1 ng satisfactorily. In addition, data obtained by the Coulson electrolytic conductivity (CD) detector, as employed by Westlake *et al.* (1970) and Patchett (1970), are presented. While both detectors appear to have similar sensitivity under our experimental conditions, the CD has the advantage of not requiring cleanup of sample extracts.

The application of this method to the analysis of water and river and ocean sediments is being tested.

EXPERIMENTAL SECTION

Apparatus. Micro-Tek gas chromatograph, model DSS-161 with ^{63}Ni EC detector or Coulson CD detector (Tracor Analytical Instruments, Austin, Tex.) was used. A 3-ft pyrex, ¼ in. o.d., 5/32 in. i.d. column was used containing 60–80 mesh acid-washed, dimethyldichlorosilane-treated, Chromosorb W coated with 5% Carbowax 20M. Operating conditions are given in Table I.

Materials. Methanol, ethyl acetate, and hexane were nanograde or redistilled. Avoid solvents in plastic-lined containers.

Standards. Pure propazine, atrazine, and simazine were obtained from Geigy Chemical Corp., Ardsley, N. Y. Prepare 0.5 to 2.0 ppm mixtures of standards in ethyl acetate.

Alumina was neutral, 100–200 mesh, activity Grade I, Brockmann.

Description of the soils used in this study follows.

Helemano. Subgroup: Tropeptic haplustoks. Family: Clayey, kaolinitic, isohyperthermic. pH 4.5, organic matter 3–5%.

Kapaa. Subgroup: Typic gibbsiorthox. Clayey, oxidic, isohyperthermic. pH 5.3, organic matter 10.5%.

Hanalei. Subgroup: Typic fluvaquents. Very fine, oxidic, nonacid, isohyperthermic. pH 5.3, organic matter 3–4%.

Procedure. *With CD Detection.* Weigh 37.5 g of 20-mesh air dry soil into a 500-ml round-bottomed flask and add 20 ml of methanol. Mix, add 130 ml of ethyl acetate, and reflux for 30 min using a heating mantle. Cool, filter through Whatman No. 12 folded paper containing 5 g of anhydrous sodium sulfate, and collect 100 ml of filtrate. Transfer to a 400-ml beaker, add a few boiling stones, and evaporate to about 5 ml. Cool, transfer to a 10-ml volumetric flask with ethyl acetate, dilute to volume, and inject 5 μl, representing 12.5 mg of soil, into the gas chromatograph with CD detector. This method is very rapid, as cleanup is unnecessary for this detector.

With EC Detection. Proceed as above but evaporate the extract to no more than 1 ml, being careful not to evaporate to dryness. Cool, introduce 4 g of alumina, and mix thoroughly to make a dry and free-flowing mixture. Pour this into a 10 × 300 mm chromatographic column containing 8 cm of alumina topped with a 2-cm layer of anhydrous sodium sulfate. Wash beaker with small amounts of hexane and transfer washings to the column. Elute hexane solubles with a total volume of 75 ml of hexane. Application of slight air pressure may be necessary for adequate elution rate. Discard washings.

Elute the triazines off the column with 50 ml of ethyl acetate using some solvent to rinse the beaker. Evaporate to about 5 ml, cool, transfer to a 10-ml volumetric flask, and dilute to volume. Mix and inject 5 μl into the gas chromatograph.

Inject 5-μl volumes of the above standards and prepare the standard curve either with peak heights or areas. For the latter method, use the product of height and width at the half height.

RESULTS AND DISCUSSION

Choice of Solvent and Cleanup. The high sensitivity of the electron capture detector for halogenated organics precludes the use of halogenated solvents in procedures requiring this detector. Among the nonhalogenated solvents that were tested, the choice appeared to be either ethyl acetate or acetonitrile, which was employed by Mattson *et al.* (1970). While the latter solvent was suitable for dissolving atrazine and propazine, ethyl acetate appeared to be superior for simazine. The use of some methanol allowed better wetting of the sample before the addition of ethyl acetate. The analysis of moist samples may be accomplished by adding a suitable amount of sodium sulfate to the digestion flask. However, care must be taken to remove any excess moisture which may form upon evaporation of the extract. In the presence of some acidity, hydrolysis of the triazine may occur under these conditions.

The conductivity detector has the advantage of specificity for nitrogen compounds, which obviates the cleanup requirement. For electron capture detection, however,

University of Hawaii, Honolulu, Hawaii 96822.

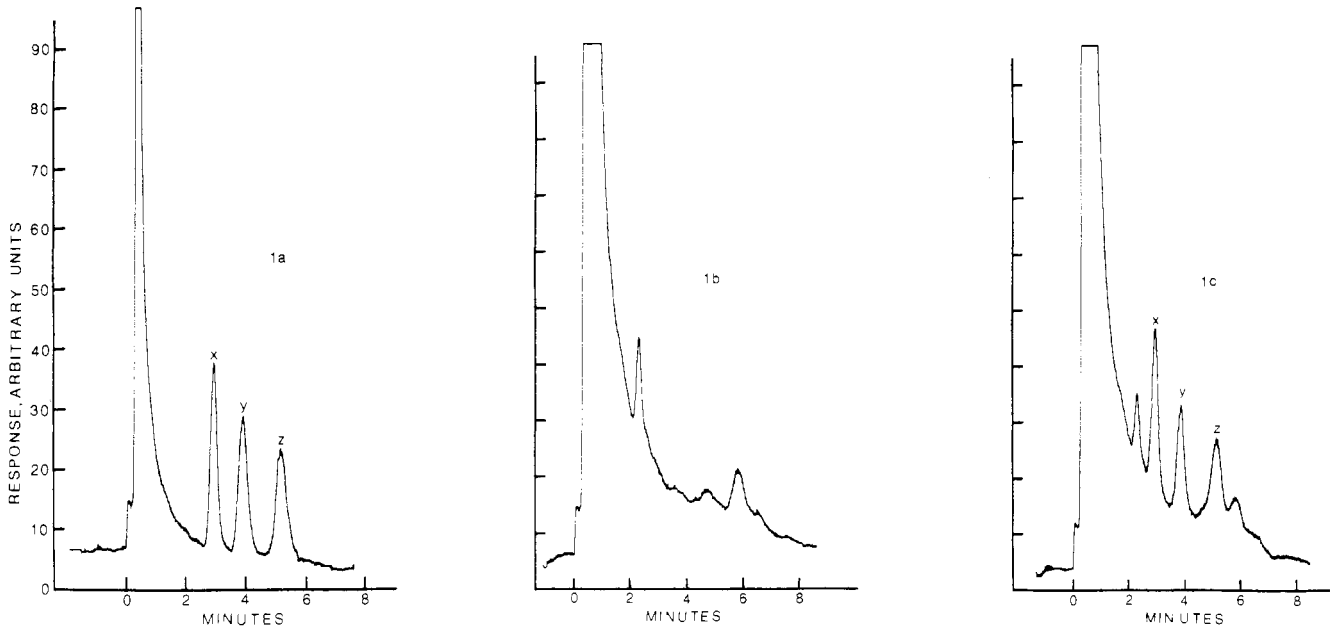

Figure 1. Chromatograms of recovery of propazine (x), atrazine (y), and simazine (z) added to Kapaa soil. a. Standards only (10 ng of each). b. Soil only. c. Standards added to soil (10 ng/12.5 mg of soil:0.80 ppm). EC detector, attenuation 16×.

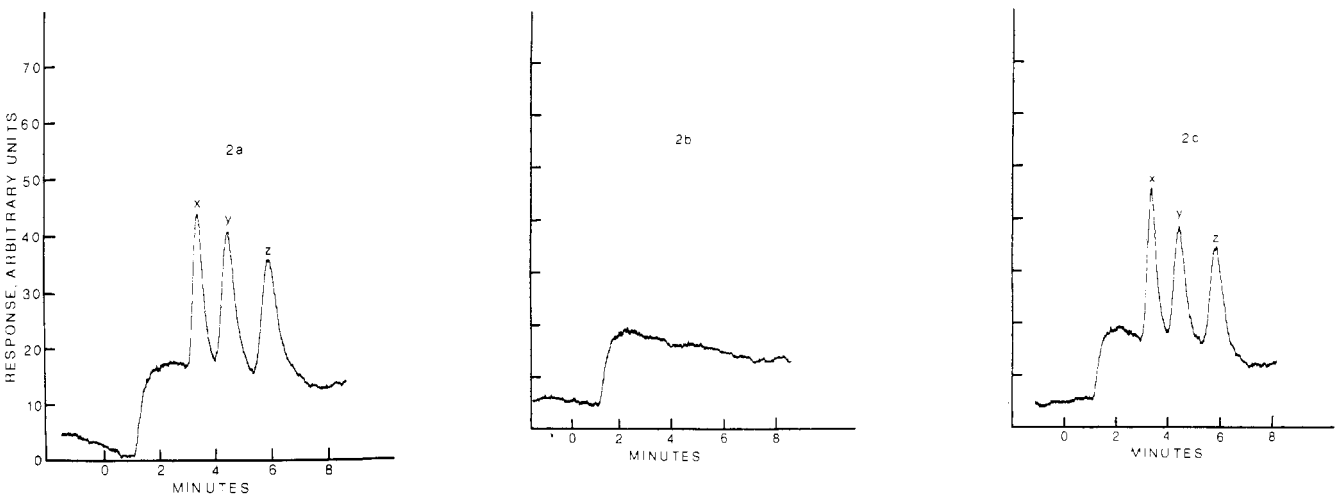

Figure 2. Chromatograms of recovery of 10 ng each of propazine (x), atrazine (y), and simazine (z) added to Kapaa soil. a. Standards only (10 ng of each). b. Soil only. c. Standards added to soil (10 ng/12.5 mg of soil:0.80 ppm). CD detector, attenuation 1×.

Table I. Gas Chromatograph Operating Conditions

	EC	CD
Gas flow rates		
Carrier	30 ml/min, N_2	60 ml/min, A
Sweep	70 ml/min	20 ml/min, A
Reducing		75 ml/min, H_2
Temperatures		
Column	195°	195°
Injection port	240°	240°
Transfer line		250°
Pyrolyzer		820–850°
Detector	300°	Room T
Detector operation	DC mode	N reductive mode
Attenuation	4×10^{-10} A	1
Voltage	20 V	30 V
Chart speed	0.5 in./min	0.5 in./min
Recorder	Microcord, model 44 (⅔ sec, 1 mV)	Microcord, model 44 (⅔ sec, 1 mV)

cleanup was essential to avoid interferences. The prescribed ratio of alumina to ethyl acetate extract concentrate permitted retention of the triazines on the column. Increasing the volume of concentrate resulted in some loss of propazine upon elution by hexane. The hexane wash effectively removed most of the interferences from soil. However, some unknown though noninterfering peaks were still apparent (Figure 1, b,c).

Gas Chromatograph Parameters. The polar Carbowax 20M possessed the desired properties for separating the triazines with good resolution(1). The use of Reoplex 400 on Gas Chrom Q (Mattson *et al.*, 1970; Westlake *et al.*, 1970) gave equally good results. Trials with the nonpolar silicone DC 200 showed no resolution for the three chloro-*s*-triazines and with the intermediate-polar QF1, separation was slight, retention time being only 0.1 min apart. The specified solid support gave satisfactory results.

Both detectors showed similar sensitivity, as seen in Figures 1 and 2. While either nitrogen for DC operation or argon–methane in the pulsed mode may be used for EC

Table II. Recovery of Cl-s-triazines Added to Soil

	Soil	Triazine added, ppm	Triazine recovered, ppm	Recovery, %
	EC detector			
Propazine	Helemano	0.32	0.34	106
	Helemano	0.64	0.66	103
	Kapaa	0.16	0.16	100
	Kapaa	0.80	0.75	94
	Kapaa	1.60	1.34	84
Atrazine	Helemano	0.32	0.34	106
	Helemano	0.64	0.54	84
	Kapaa	0.16	0.18	112
	Kapaa	0.80	0.71	89
	Kapaa	1.60	1.34	84
Simazine	Helemano	0.26	0.24	92
	Helemano	0.52	0.46	88
	Kapaa	0.16	0.15	94
	Kapaa	0.80	0.71	89
	Kapa	1.28	1.08	84
	CD detector, Kapaa soil			
Propazine		0.16	0.15	94
		0.40	0.44	110
		0.80	0.82	103
Atrazine		0.16	0.14	88
		0.40	0.39	98
		0.80	0.79	99
Simazine		0.16	0.14	88
		0.40	0.37	93
		0.80	0.77	96

detection, the former is preferred. High purity of these gases was essential for detection of small amounts of herbicide. Since detector temperature also greatly affected sensitivity, a temperature of 300° is recommended. As high as 350° was tried without any apparent degradation of the chloro-s-triazines. As baseline stability was good (Figure 1), a twofold increase in sensitivity may be attained by decreasing attenuation. Under these conditions, 10 ng of either chloro-s-triazine gave approximately half-FSD. A contaminated detector may generally be cleaned by heating for 3 hr at 400°. Williams (1968) recommends using steam.

The conductivity detector usually gave broader peaks than the electron capture. For this reason conditions were sought which would result in as short a retention time as possible. Besides oven temperature and carrier flow rate, a very important parameter was column length, particularly in the 1–10 ng range. A 4-ft column gave lower and broader peaks than a 3-ft one at the same flow rate and temperature. The EC detector peaks did not appear to be affected as much by such a difference in column length. This is doubtless due to the instantaneous response of this detector as compared to the CD detector, which depends first on the conversion of the triazine to ammonia in the furnace. For this reason an increased carrier flow rate was necessary for CD detection to give retention times similar to those given by EC detection. Retention time was approximately 3 min for propazine, followed by atrazine and simazine, at about 1-min intervals. By using a 0.5-mV recorder setting, a twofold increase in sensitivity may be attained with the CD detector, as baseline was very stable. Under these conditions, 10 ng of either chloro-s-triazine gave approximately half-FSD.

The obvious advantage of the CD detector is freedom from extraneous peaks and possible interferences. Decreased sensitivity is usually corrected by following the prescribed directions for changing the strontium hydroxide scrubber, checking water quality, or reconditioning the nickel catalyst by treatment with 6 *N* nitric acid until a faint green color was apparent in the acid was helpful in restoring the activity of the catalyst. An unexpected cause of low sensitivity was traced to clogging of the capillary tubing at the detector by fine particles of resin. This was indicated by reduced water flow over the electrodes or through the overflow tube. Clogging was overcome by overnight soaking with chromic acid.

Recovery. Recovery of chloro-s-triazines added to two Hawaiian soils described above is given in Table II. One-milliliter volumes of ethyl acetate solutions containing 6–60 ppm of triazines were added to soil samples in digestion flasks, mixed thoroughly, and then processed as described above. Typical chromatograms are shown in Figures 1 and 2. The recovery values by the EC detector ranged from 84 to 112% and by the CD detector were 88–110%.

The three Hawaiian soils described above, having an indefinite previous history of pesticide application, have been analyzed and found to contain nondetectable levels of chloro-s-triazines. Four unknown peaks were evident in the EC but not in the CD chromatograms. This was consistent for the three soils. An EC chromatogram of one of the hexane washings obtained in the cleanup step showed a large number of unknown peaks.

LITERATURE CITED

Burke, J., Holswade, W., *J. Ass. Offic. Anal. Chem.* **49,** 374 (1966).
Cochrane, W. P., Wilson, B. P., *J. Chromatogr.* **63,** 364 (1971).
Mattson, A. M., Kahrs, R. A., Murphy, R. T., *Residue Rev.* **32,** 371 (1970).
Patchett, G. G., *J. Chromatogr. Sci.* **8,** 55 (1970).
Purkayastha, R., Cochrane, W. P., *J. Agr. Food Chem.* **21**(1), 93 (1973).
Westlake, W. E., Westlake, A., Gunther, F. A., *J. Agr. Food Chem.* **18,** 685 (1970).
Williams, I., *J. Ass. Offic. Anal. Chem.* **51,** 64 (1968).

Received for review October 24, 1972. Accepted February 9, 1973. Published with the approval of the Director, Hawaii Agricultural Experiment Station as Journal Series No. 1535. Since this paper was submitted for publication, a report by Purkayastha and Cochrane (1973) describing a comparison of electron capture and conductivity detectors for residue analysis of atrazine in water, soil, and corn has appeared in this journal.