A Low Temperature Cleanup Procedure for Triazine Herbicides in Root Crops

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INTRODUCTION

The use of low temperature precipitation as a cleanup technique of pesticide residues in sample extracts prior to gas-liquid chromatographic (glc) analysis has been well documented. The procedure has been used for sample cleanup for chlorinated hydrocarbon insecticides such as methoxychlor (FAIRING and WARRINGTON 1950), methoxychlor, dicofol and DDT (ANGLIN and MCKINLEY 1960), and dieldrin, endrin, heptachlor, aldrin, isobenzan and lindane (McKINLEY and SAVARY 1962) in a variety of sample materials. The technique has been extended to include a number of organophosphorus pesticides in plant samples (BATES 1965). The low temperature cleanup of hexane extracts of grains, soils and other sample types has been examined recently GRUSSENDORF et al. 1970). MCLEOD and WALES (1972) reported on the evaluation of a low temperature cleanup technique that separated both polar and apolar pesticide residues from sample lipids, waxes and water in a single step. Recovery data for this procedure were presented for a number of insecticides, herbicides and fungicides.

In the present work, the application of this technique, with some modification, to the analysis of triazine herbicides in root crops was examined and the evaluation of the Coulson conductivity detector and the pulsed Ni^{63} electron-capture (ec) detector for glc analysis of the extracts was carried out. This work was part of an investigation to evaluate the low temperature precipitation method as a multiresidue cleanup technique in conjunction with an automated multi-detector glc system.

MATERIALS

Apparatus: A Micro-Tek gas chromatograph (MT 220, Tracor Inc.) was fitted with a Coulson conductivity detector (Tracor) and a pulsed nickel-63 electron capture detector (Tracor). The splitting ratio of the glc effluent stream was 1:6.5 in favor of the Coulson. The 3ft x 1/8in. i.d. borosilicate glass column was packed with 5% OV-17 on chromosorb W/HP (80/100 mesh).

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Operating parameters were as follows: helium, 107ml/min; nitrogen enrichment to ec detector, 90ml/min; isothermal oven temperature, 210°C; temperature program, 130°C hold for 2 min followed by a 6°C/min rise to 235°C and a 10 min hold; injection port temperature, 210°C; ec detector temperature, 285°C; Coulson furnace temperature, 780°C; Coulson hydrogen flow (reductive mode), 60 ml/min; Coulson bridge potential, 30 V and IX attenuation; ec attenuation, $4x10^2$.

The low temperature precipitation cleanup was carried out in a cold bath apparatus described in detail by MCLEOD (1972) and MCLEOD and WALES (1972).

Reagents. All organic solvents were pesticide grade, residue free materials. The extraction solvent consisted of acetone/benzene/1N H_2SO_4 (190+10+5) per 50 g sample. The Solka Floc filter aid was acetone washed before use.

Stock solutions of the triazines (atrazine, 2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine and simazine, 2-chloro-4,6-bis(ethylamino)-s-triazine) were prepared by dissolving 25 mg in methanol and diluting to 25 ml. For spiking purposes the stock solutions were serially diluted.

ANALYTICAL PROCEDURE

Sample Extraction. Fifty grams of the spiked crop tissues were extracted by blending for 5 min, twice, with fresh 100 ml portions of the extraction solvent. The supernatants were recovered by suction filtration through a medium porosity fritted glass funnel, combined and made to 250 ml with acetone.

Low Temperature Precipitation. The low temperature precipitation was carried out according to MCLEOD and WALES (1972) with the exception that ethanol was chosen as the cooling liquid as opposed to methanol since ethanol fumes pose a significantly lower health hazard. For low levels of herbicides the final 3 ml extracts were concentrated to 2.0, 1.0 and 0.5 ml as necessary.

GLC Analysis. Between 2 and 5 µl aliquots of the cleaned up extracts were analysed by glc. The pesticide recoveries were calculated by comparing the peak heights of the herbicides in the samples to those of the standards.

RESULTS AND DISCUSSION

The use of acetone/benzene/1N H_2SO_4 (190+10+5) as the extraction solvent for the low temperature cleanup was better for the polar pesticides than the original acetone+benzene (19+1) solvent (MCLEOD and WALES 1972). The addition of the sulfuric acid did not decrease the efficiency of extraction of the less polar compounds such as the chlorinated hydrocarbons (MCLEOD 1973).

The cleaned up extracts varied in color from colorless for potatoes to a definite yellow-orange for carrots. The filtrates from the low temperature precipitation of the beet samples were pink. However, the colour was removed upon passing through the sodium sulfate column.

Figure 1 shows the results obtained for carrots and parsnips containing 0.1 ppm of atrazine. The results of the Coulson detector may be quantitated while the ec chromatograms could not be analysed. The quantitation of triazines in beets and turnips at levels of less than 1 ppm could not be made with either detector. The results were greatly improved when the extracts for glc were evaporated to dryness and redissolved in hexane. This treatment resulted in much of the residual matter remaining as a solid in the bottom of the centrifuge tubes. Figure 2 compares the results of atrazine in turnip before and after the hexane transfer step. The great majority of the interferences were removed by using the hexane. Recoveries of the triazines at the levels studied were not affected by this treatment. (For more volatile pesticides the residue should not be taken to complete dryness).

Under the conditions used, the triazine peaks appeared near the solvent front when run isothermally. Temperature programming, however, provided a much better separation of sample components. Figure 3 compares the temperature programmed results with isothermal data obtained for 0.1 ppm of atrazine in beets using the Coulson detector. Similar improvements in the chromatograms were also obtained for the ec detection. The rise in baseline during temperature programming with the Coulson detector may be attributed to the temperature increase in the deionized water caused by the rising temperature of glc effluent or to the change in effluent flow rate.

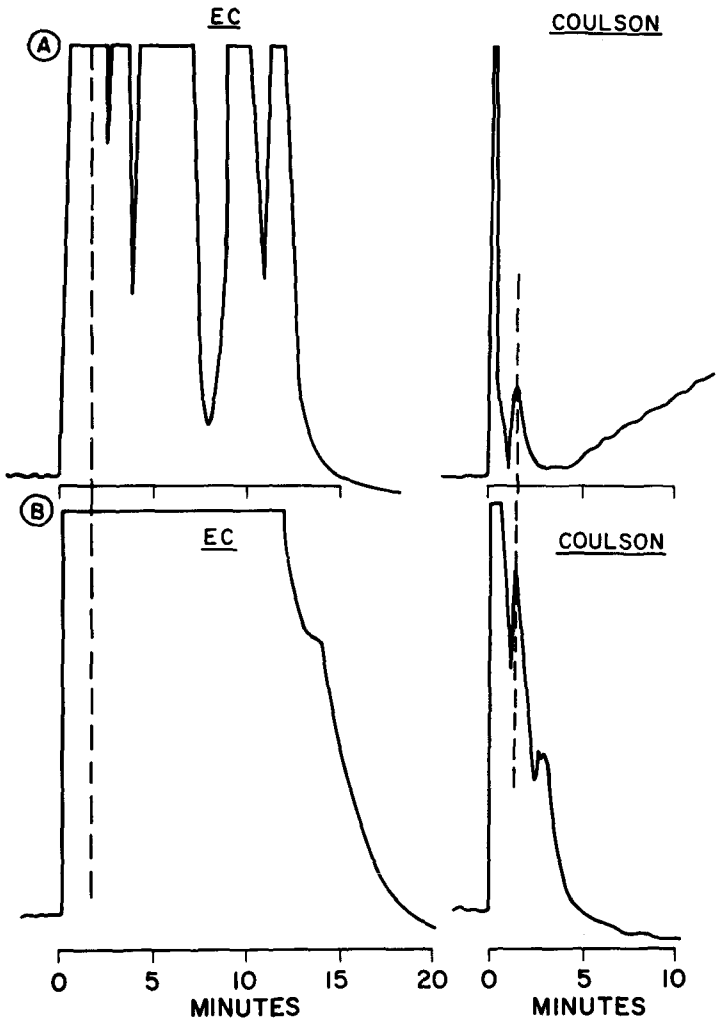

Figure 1. Comparison of responses from the ec and Coulson detectors for: (A) 0.1 ppm atrazine in carrots; (B) 0.1 ppm atrazine in parsnips. Dashed lines indicate the position of the atrazine peak.

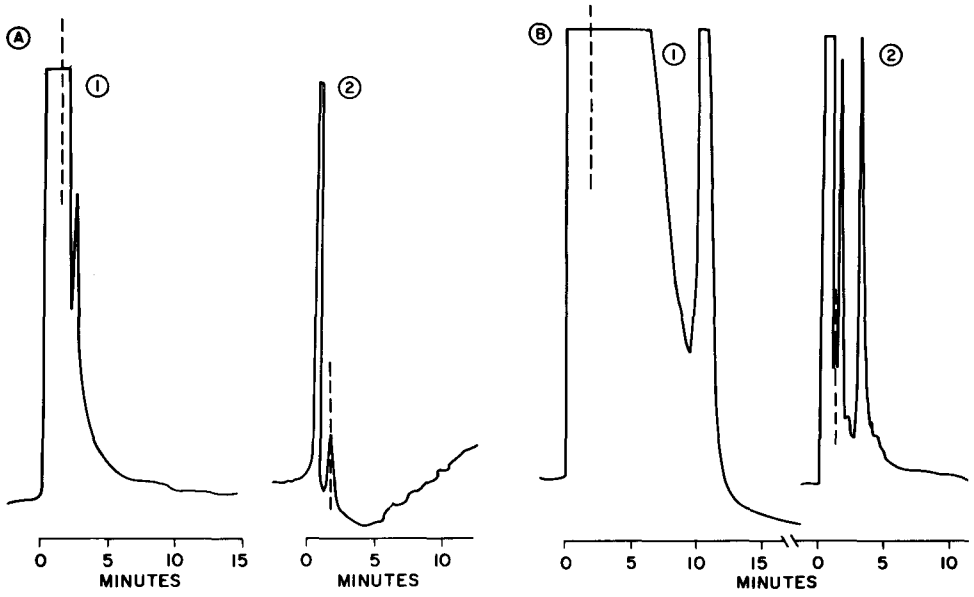

Figure 2. Comparison of glc results before and after the transfer of the residue to hexane. (A) Coulson results: 1. 10 mg turnip at 0.4 ppm atrazine before hexane transfer; 2. 20 mg turnip at 0.1 ppm atrazine after hexane transfer. (B) ec results: 1. 10 mg of turnip at 0.4 ppm atrazine before hexane transfer; 2. 20 mg turnip at 0.1 ppm atrazine after hexane transfer. Dashed lines indicate the position of the atrazine peak.

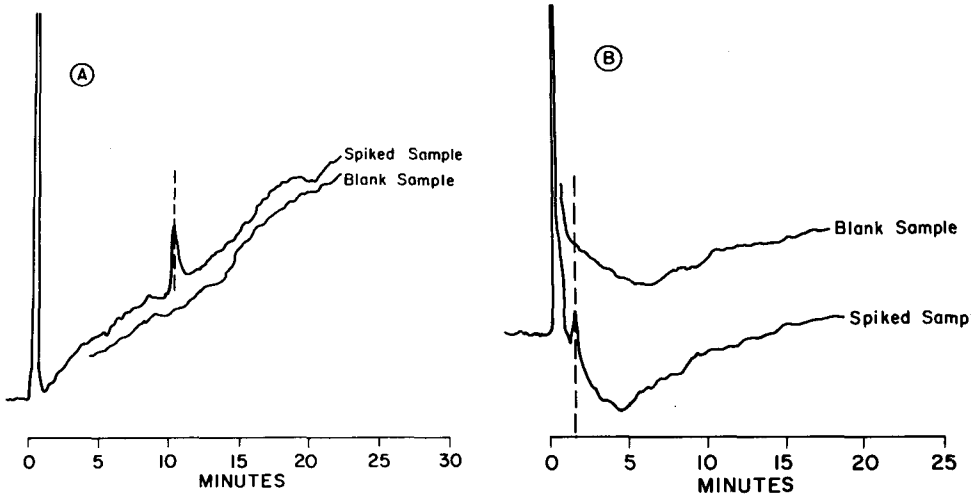

Figure 3. Comparison of temperature programming and isothermal results for 0.1 ppm atrazine in beets. (A) temperature program. (B) isothermal at 210°C. Dashed lines indicate atrazine peak.

Table I shows the recoveries obtained using the Coulson after the low temperature cleanup and hexane transfer for atrazine and simazine at a variety of concentrations in the samples. Recoveries were generally good at all levels examined.

TABLE I

Recoveries of the Triazines

Sample	Triazine, ppm	% Recoveries
Potatoes	Atrazine, 2.0	100, 102, 85
	0.4	85, 90, 75
	0.2	100, 122
	Simazine, 2.0	89, 87
Carrots	Atrazine, 2.0	100, 95, 90
	0.4	94, 90, 105
	0.1	130, 100, 68
	Simazine, 2.0	100, 100
Parsnips	Atrazine, 2.0	100, 88, 93
	0.4	101
	0.1	100, 80, 78
	Simazine, 2.0	100
Beets	Atrazine, 0.1	120, 80
	Simazine, 2.0	100, 105
Turnips	Atrazine, 0.1	90, 81, 100
	Simazine, 2.0	94, 71

The cleanup technique proved to be suitable for multi-sample analysis with nitrogen specific detection. The OV-17 column performed well for 122 sample injections which varied from 10-50 mg of equivalent crop material per injection. Even after this time only the glass wool plug at the inlet of the column needed to be replaced.

CONCLUSIONS

Crop extracts of the triazine herbicides, atrazine and simazine, were suitably cleaned up by low temperature precipitation for glc and nitrogen detection. The use of this technique as a multi-residue cleanup method for the glc screening of pesticides may be extended to include these and other similar triazine herbicides. The ec detector

was found to be unsuitable for triazine analysis using the low temperature cleanup technique on the crops studied.

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