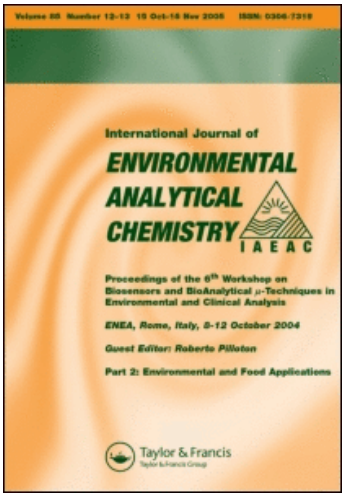

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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To cite this Article Lawrence, J. F.(1978) 'Evaluation of Electrolytic Conductivity Detection for the Gas Chromatographic Analysis of Six Polar Organonitrogen Herbicides', International Journal of Environmental Analytical Chemistry, 5: 2, 95 — 101
To link to this Article: DOI: 10.1080/03067317808071135
URL: http://dx.doi.org/10.1080/03067317808071135

Intern. J. Environ. Anal. Chem., 1978, Vol. 5, pp. 95–101

Printed in Great Britain

Evaluation of Electrolytic Conductivity Detection for the Gas Chromatographic Analysis of Six Polar Organonitrogen Herbicides

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(*Received June 5, 1977*)

The Coulson electrolytic conductivity detector (nitrogen mode) was evaluated for the detection in foods of six polar organonitrogen herbicides containing phenolic or carboxyllic moieties. The herbicides were extracted from the crop materials with acetone and partitioned between water and dichloromethane/hexane (1 : 1). The organic extract was reduced in volume and treated with ethereal diazomethane. The methylated products were then cleaned up on a 2% deactivated Florisil column and analysed by gas chromatography. Detection limits ranged from 0.01–0.1 ppm depending upon type of crop and herbicide. Recovery studies indicated that the extraction procedure removed 40–90% of added herbicide, from the foods at 0.1 and 1.0 ppm.

KEY WORDS: Electrolytic conductivity, gas chromatography, organonitrogen herbicides, foods.

INTRODUCTION

The Coulson (or more recently the Hall) electrolytic conductivity detector (CEC) is a selective detector useful for the gas chromatographic analysis of organonitrogen (nitrogen mode) or organohalogen (halogen mode) compounds. Although the electron capture (EC) detector is generally more sensitive than the CEC, the selectivity of the latter to nitrogen or halogen compounds is much superior which can make it more suitable in many instances for analysis of food or other environmental samples where coextracted material is significant. Comparisons between the two detectors have shown that the CEC can be superior for triazine analysis[1] and similar to

EC for analysis of diethylstilbestrol derivatives.[2] Another advantage of the CEC is that the sensitivity to compounds is easier to predict than EC, and is based on the percent nitrogen or halogen contained in a compound. Efforts to improve the sensitivity of the CEC have been carried out by several workers[3-6], and although successful, they still do not approach the sensitivity of the EC detector.

Since a large number of herbicides contain nitrogen, the CEC was thought to have much potential for their detection in food samples, especially for compliance (regulatory) purposes where, usually, 0.1 ppm detectability is adequate. Methods have been developed at these levels for triazines,[7] phenyl carbamates and ureas[8] and others including thiocarbamates.[9] The present report describes results obtained from the analysis of six polar herbicides spiked in several foods. Since these compounds chromatographed poorly or not at all directly, the methyl ether or ester derivatives were formed by reaction with diazomethane before analysis.

EXPERIMENTAL

Apparatus

A Microtek Model MT 220 (Tracor Inc., Austin, Texas) equipped with a Coulson conductivity detector in the nitrogen mode was used for the analyses. Chromatography columns were constructed from 1.3 meter × 4 mm id borosilicate glass and packed with 4% SE-30/6% SP-2401 on Chromosorb W/HP (80-100 mesh). Operating conditions were: carrier (helium) flow rate, 60 ml/min; sweep gas, 60 ml/min; hydrogen, 40 ml/min; injection port temperature, 240°C; transfer line, 230°C; furnace, 820°C. The d.c. voltage was set to 60 V instead of the normal 30 V which produced about a two-fold increase in sensitivity of our detector.[6] However, because of the general lack of sensitivity of our particular cell, the results at 60 V are comparable to most other Coulson results at 30 V. The column temperature was varied from 190°-200°C depending upon compound analysed.

Reagents

All solvents were glass-distilled residue-free grade. The Florisil was prepared by activating 100 g at 130°C overnight, cooling and mixing with 2 ml H_2O in a sealed glass jar. The jar was mechanically shaken for 6 hr and permitted to stand overnight before use. The excess was stored in well sealed glass jars. The herbicides studied were bentazon (3-isopropyl-2,1,3-benzothiadiazinon-(4)-2,2-dioxide), bromoxynil (3,5-dibromo-4-hydroxy-benzonitrile), chloramben (3-amino-2,5-dichlorobenzoic acid), dinoseb (2-sec-butyl-4,6-dinitrophenol), DNOC (2-methyl-4,6-dinitrophenol) and ioxynil (4-hydroxy-3,5-diiodobenzonitrile). Solutions of these were prepared in acetone (1 mg/ml) and

serially diluted as required. The foods examined were carrot, cabbage, corn, pea and potato.

Preparation of Diazomethane

The diazomethane reagent was prepared from 0.5 g Diazald® (N-methyl-N-nitroso-p-toluenesulfonamide, Aldrich, Milwaukee, Wis., U.S.A.) in 20 ml ether in the presence of 3.0 g carbitol and 3 ml 60% aqueous KOH. The diazomethane was collected by bubbling nitrogen through the reaction mixture and into 30 ml of ice-cooled anhydrous ether which retained the diazomethane. The resulting solution was stable when refrigerated for 3–4 days.

Sample Extraction

A 35 g portion of representative chopped, washed food sample was spiked with a herbicide and blended with 100 ml of acetone for 4 min in a Sorvall homogenizer at medium speed. The homogenate was suction-filtered through a 150 ml medium porosity sintered-glass funnel into a 500 ml flask. The filter cake was rinsed with 15 ml of acetone. The total filtrate was transferred to a 500 ml separatory funnel containing 100 ml each of hexane and dichloromethane. The funnel was shaken for 1 min then the lower aqueous phase was withdrawn into a 250 ml separatory funnel containing 15 ml saturated sodium chloride solution. The aqueous contents were extracted twice with 70 ml volumes of dichloromethane. All organic extracts were then combined and dried by the addition of 2 gm anhydrous Na_2SO_4 and permitted to sit for at least 15 min. The extract was passed through a 150 ml sintered glass funnel into a 1000 ml round-bottom flask. The Na_2SO_4 was rinsed with 15 ml dichloromethane and the washings collected in the same flask. The extract was concentrated by rotary evaporation at ambient temperature to about 1–2 ml (being cautious not to allow the extract to evaporate to dryness, since herbicide losses will occur).

Methylation

The sample residue was transferred to a 20 ml test tube with PTFE-lined screw-cap, and evaporated at ambient temperature to about 0.2 ml under a gentle stream of nitrogen. Following this, 6 ml of the diazomethane solution were added, the test tube capped and permitted to stand at room temperature for at least 5 min. After this time the cap was removed and the solution evaporated to 1.0 ml under nitrogen at ambient temperature. A 10 ml volume of hexane was added and the solution transferred to a Florisil column for cleanup.

Florisil Cleanup

The column consisted of a 2.0 cm id glass tube, dry packed with 20 g Florisil (2% deactivated) and covered with a 0.25 inch layer of anhydrous Na_2SO_4. Once the methylated extract was on the Florisil, the column was eluted sequentially with 100 ml of 30% dichloromethane in hexane followed by 100 ml of 15% acetone in hexane. The first elution was discarded since the latter fraction contained the methylated pesticides. This fraction was evaporated to about 3 ml and transferred to a 5 ml centrifuge tube and further evaporated to 2 ml for gas chromatographic analysis.

TABLE I

Retention times and detectability of some organonitrogen herbicides

Herbicides	Retention time (min)	Column temp. (°C)	Detectability[a]
chloramben	2.8	200	8
bentazon	5.7 (4.5)	190 (200)	8
bromoxynil	3.3 (2.4)	190 (200)	9
dinoseb	4.7	200	4
DNOC	3.3	200	3
ioxynil	3.9	200	35

[a]Nanograms required to produce a 2 cm peak at 1 × attenuation, 60 V, at the retention times shown.

RESULTS AND DISCUSSION

Table I lists retention times and detectability of the methylated herbicides. The dinitrophenols, dinoseb and DNOC, were about twice as sensitive as chloramben, bentazon and bromoxynil due to the presence of two nitrogen atoms in the former as opposed to only one in each of the latter compounds. Ioxynil consistently produced a much smaller peak than might be expected. The SE-30/SP-2401 column performed well for the rest of the herbicides.

The methylation reaction produced very consistent results even between diazomethane preparations. Extraneous material in the sample extracts did not hinder the conversion of the herbicides to their methyl derivatives as evidenced by spiking blank sample extracts just before the reaction and comparing peak heights to similarly treated standards. The effect of water on the reaction was also studied by comparing reactions on standards in the presence of 1, 2, 3 or 10 drops of water from a Pasteur pipet. No effects on the yield of products were observed for any of the water additions under the reaction conditions used.

The extraction and cleanup procedure is similar to that described earlier[9] for the direct analysis of several other less polar herbicides. The present compounds would not appear in the 15% acetone in hexane fraction in their underivatized form due to the polar nature of the phenolic and carboxyllic moieties. The cleanup was adequate for the detection of most of the compounds studied down to at least 0.1 ppm. Figures 1 and 2 show several

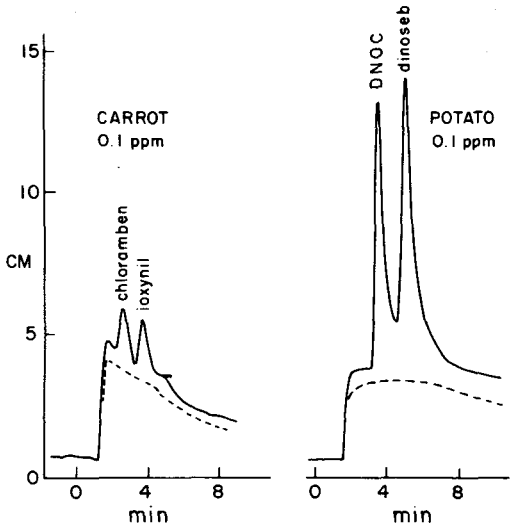

FIGURE 1 Chromatograms of carrot and potato spiked at 0.1 ppm with chloramben and ioxynil, DNOC and dinoseb, respectively. Glc condictions as described in Table I. Attenuation 1X; 35 mg of equivalent sample injected. Dashed line indicates sample blank.

examples of chromatograms obtained for the herbicides spiked in some of the foods studied. The carrot and potato samples were very clean and all herbicides could be easily detected at the 0.1 ppm level. However, corn provided a high background after venting the solvent front and made detection below 0.3 ppm for ioxynil, chloramben, bromoxynil and bentazon difficult. Ioxynil, chloramben and DNOC could not be detected at 0.1 ppm in cabbage due to the presence of an interfering peak which had a retention time the same as DNOC and equivalent to about 0.05 ppm DNOC. The percent recoveries of the compounds studied averaged 65% for bentazon, 65% for bromoxynil, 65% for DNOC, 61% for dinoseb, 84% for ioxynil and 43% for chloramben. These were the averages of at least four extractions from various crops at both 0.1 and 1.0 ppm. Recoveries with the exception of ioxynil were considered less than satisfactory for quantitative purposes. The volatility of both parents and methylated products is such that much caution must be

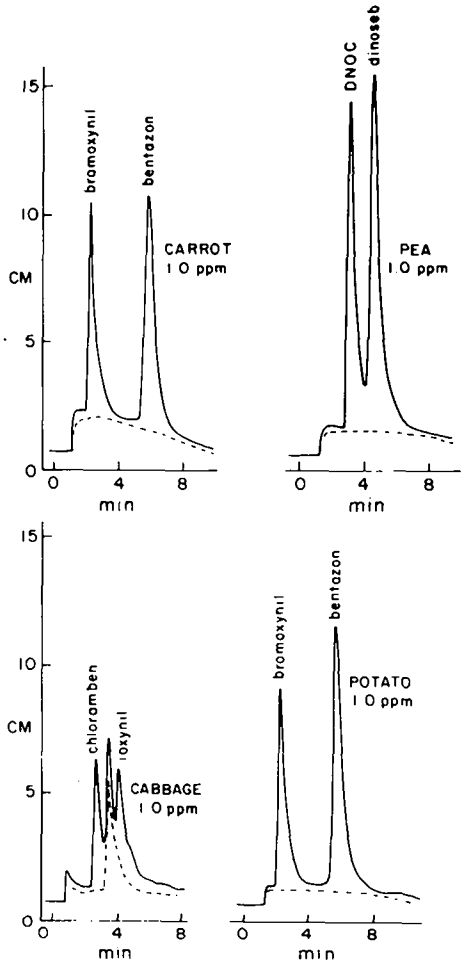

FIGURE 2 Chromatograms of various foods spiked with the herbicides at 1.0 ppm. Glc conditions as described in Table I. Attenuation 1X; 35 mg of equivalent sample injected. Dashed line indicates sample blank.

exercised in all evaporation steps. Also, being of a polar nature adsorption to glass surfaces may also account for some losses. This might be especially true for chloramben which contains both an amino and carboxyllic acid moiety. However, even though these effects were not studied, the method as such appeared well suited for detection of the herbicides for screening purposes in most of the foods studied at levels down to 0.01-0.1 ppm.

The Coulson detector proved to be completely reliable throughout this

work. Only the strontium hydroxide scrubber and ion-exchange resin required changing about once a month depending upon the degree of contamination. Sample interferences usually manifested themselves as high baselines after venting (Figures 1 and 2) the only exception being a single interfering peak in the cabbage samples.

CONCLUSION

The Coulson conductivity detector was found to be well suited for polar organonitrogen herbicide residue screening. The combined sensitivity and selectivity of the detector permits the detection of a variety of herbicides at levels of 0.01–0.1 ppm in several food crops.

Acknowledgement

The author expresses his appreciation to Davida Turton for carrying out the analyses.

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