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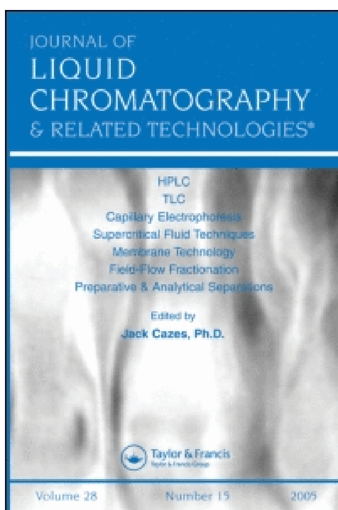

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THE DETERMINATION OF THE HERBICIDE LINURON IN SASKATOON BERRIES USING HPLC WITH COLUMN SWITCHING

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ABSTRACT

A sensitive method for the determination of residues of the herbicide linuron [3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea] in saskatoon berries (Amelanchier anifolia Nutt.) is described. Use of column switching techniques permitted a limit of quantification of 10 µg/kg. Recoveries at the 10 µg/kg fortification level were in the order of 86%.

INTRODUCTION

The saskatoon shrub (Amelanchier anifolia Nutt.) grows one to seven meters in height and produces a berry about 1 cm in diameter which is either blue-purple or white (A. anifolia Nutt. f. alba Neilsen). It is presently grown commercially in the provinces of Alberta and Saskatchewan, Canada, with the fruit being processed into jams, jellies and syrups etc. In commercial plantings, application of herbicides is the preferred method for

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weed control. In recent studies (1-4), established saskatoons have demonstrated good crop tolerance to fall or early spring applications of linuron [3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea] when applied as directed basal sprays at 2-6 kg/ha. However, no information is available regarding possible linuron residues in the ripened fruit following these treatments. Thus, the present study was initiated to determine whether residues of linuron were present in the ripened fruit after early spring applications of linuron at 4 kg/ha. The application rate studied was the maximum rate which would appear on the container label if the use was subsequently registered.

MATERIALS

Chemicals

All solvents were pesticide or HPLC grade (BDH Chemicals). Florisil (Fisher Scientific Co.,), 60-100 mesh, was heated at 600 C for 24 h and then deactivated by the addition of 2% water (w/w). Water, used for liquid chromatography, was passed sequentially through a 0.45 μ filter (Millipore, type HA) and a C18 Sep-Pak (Millipore-Waters; 1 L of water per Sep-Pak). After mixing the water with methanol (40/60; v/v), the mobile phase was filtered through a 0.45 μ nylon filter (Fisher Scientific Co.). Linuron was obtained as a reference standard from the Environmental Protection Agency, Triangle Park, N.C.

Apparatus

A Waters liquid chromatography system was used consisting of two Model 510 pumps, each of which delivered mobile phase at a flow rate of 1 mL/min; the WISP Model 710B autosampler, set to inject 100 μL; the Model 490 programmable multiwavelength detector set at 248 nm; and the Model 840 data system. The chromato-

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graphy was carried out using a 25 cm x 3.9 mm i.d. μBondapak 10 μ C18 column (Waters Associates), a 10 cm x 3.9 mm i.d. NovaPak column (Waters Associates), and a guard column, 23 mm x 3.9 mm i.d., which was packed with Bondapak 37-50 μ C18 Corasil (Waters Associates). All three columns, in configuration with three Waters automated switching valves as illustrated in Figure 1, were housed in an oven maintained at 40 C.

METHODS

Herbicide Treatments

Linuron applications were made to established saskatoon plantings at four locations in the Canadian prairies: the Alberta Horticultural Research Center at Brooks, Alberta; a commercial planting near Carstairs, Alberta; the Agriculture Canada Prairie Farm Rehabilitation Administration Tree Nursery at Indian Head, Saskatchewan; and the Agriculture Canada Research Station at Morden, Manitoba. At each location, both the treated and check plots were replicated four times in a randomized complete block. In early spring, linuron was applied at 4 kg/ha as a directed basal spray using CO_2 pressurized hand held booms. One pass was made on each side of a plot such that the spray overlapped in the center of the plot. Developmental stages of the saskatoons at the four locations ranged from before leaf bud break to past flowering.

Sampling

Samples were collected at each location by randomly hand picking from each bush within a plot. Picking was carried out when sufficient berries had ripened (mid to late July) to enable collection of the desired sample size (0.5-1.0 kg). Immediately after picking, the berries were placed in polyethylene freezer bags and stored at -10 C until extraction.

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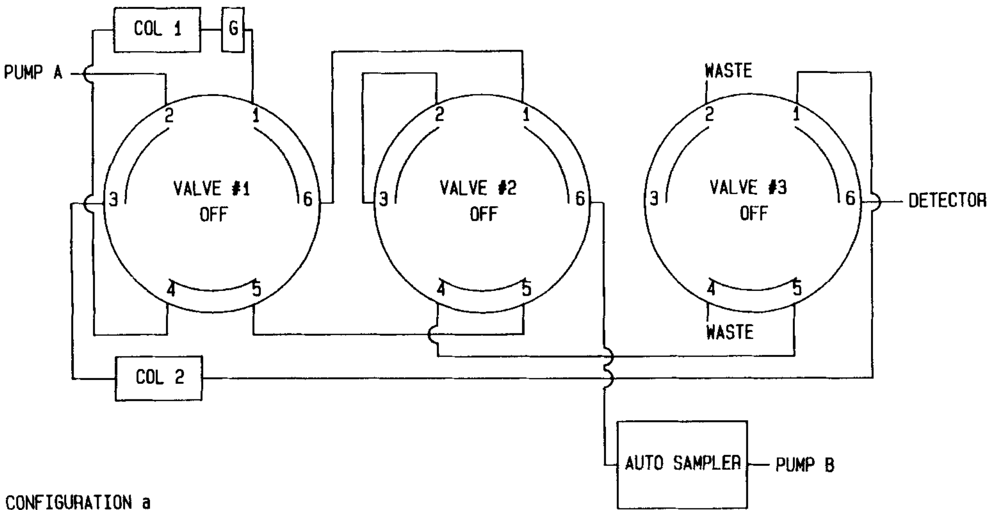

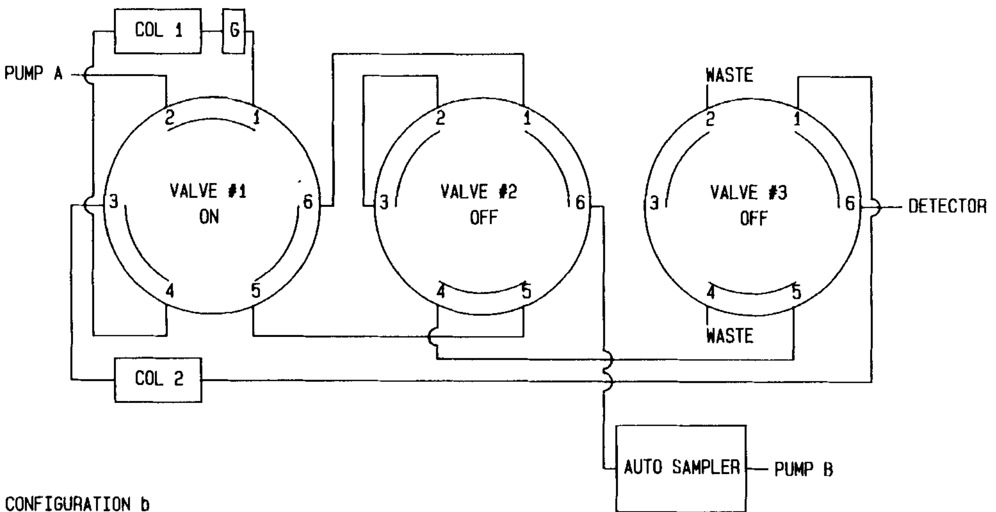

FIGURE 1. Configurations of the guard column, two analytical columns and the three automated switching valves.

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<u>Sample Extraction</u>

Saskatoon berries (50 g) and methanol (125 mL) were blended at high speed for 5 min in a 250-mL stainless steel blender jar. The blended sample was filtered under reduced pressure through a fritted glass Buchner funnel equipped with a glass fiber filter paper, and the filter cake washed twice with 25-mL methanol rinses of the blender jar. The combined filtrates were then taken to volume (200 mL) with methanol.

The methanol extract (40 mL; equivalent to 10 g of berries) was transferred to a 125-mL separatory funnel containing 50 mL of 5% NaCl solution, and the mixture was extracted three times with 25 mL of methylene chloride. Each methylene chloride extract was passed through 30 mL of anhydrous sodium sulfate (contained in a 9 cm dia. long-stemmed funnel on top of a glass wool plug) into a 250-mL round bottom flask, and the sodium sulfate finally washed with 25 mL of methylene chloride. The combined methylene choride extracts were then concentrated just to dryness using a rotary evaporator.

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<u>Florisil Column Cleanup</u>

Florisil (4 mL) was added to 10 mL of hexane contained in a 10 mm i.d. x 200 mm column and topped with 1 cm of anhydrous sodium sulfate, and the hexane drained to the surface of the sodium sulfate. The saskatoon berry extract residue was transferred to the column with three 2-mL 30% methylene chloride in hexane rinses of the 250-mL round bottom flask. The column was washed with a further 24 mL of 30% methylene chloride in hexane and the wash discarded. The column was then eluted at a rate of 1 mL/min with 25 mL of 10% acetone in hexane into a 50-mL round bottom flask. The eluate was evaporated just to dryness using a rotary evaporator. Exactly 2.0 mL of 40% aqueous methanol (v/v) was added to the 50-mL round bottom flask to dissolve the eluate

residue, and then removed using a 2.0-mL Luer-LOK tipped glass syringe equipped with a stainless steel needle. The needle was then replaced with a Luer-LOK type filter (Millex HV4 0.45 µm filter unit; Millipore Waters Cat. No. 82680) and the sample filtered directly into an autosampler vial.

Injection of the sample occurred when the switching valves were in configuration a, Figure 1. The retention time of linuron on the first analytical column (µBondapak, Col 1) was 8.52 min and the switching valve was moved from configuration a to configuration b at 8.20 min until 9.10 min to transfer the linuron peak to the second analytical column (Nova-Pak, Col 2), at which time the valve was moved back to and remained in configuration a until the switching operation of the next injection. The linuron peak eluted from the second column at 13.20 min with the total run time being 15 min.

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Fortification Experiments

Recoveries of linuron were determined by the extraction of saskatoon berries fortified at 100, 50 and 10 µg/kg. Linuron (5.0, 2.5 or 0.5 µg in 2 mL methanol) was added to 50 g crushed untreated berries contained in a 100 mm dia. x 80 mm glass storage dish. After the methanol had evaporated, the storage dish was capped and placed in a freezer for at least 24 h prior to extraction. Each fortification level was replicated 5 times.

RESULTS AND DISCUSSION

The extraction procedure used in the present study was a modification of that (5) for the extraction of several urea herbicides, including linuron, from a number of different vegetables. Aqueous methanol, which has been used by several workers (6,7,8) as the mobile phase in the HPLC detection of urea herbicides, was pumped through both analytical columns. Use of the

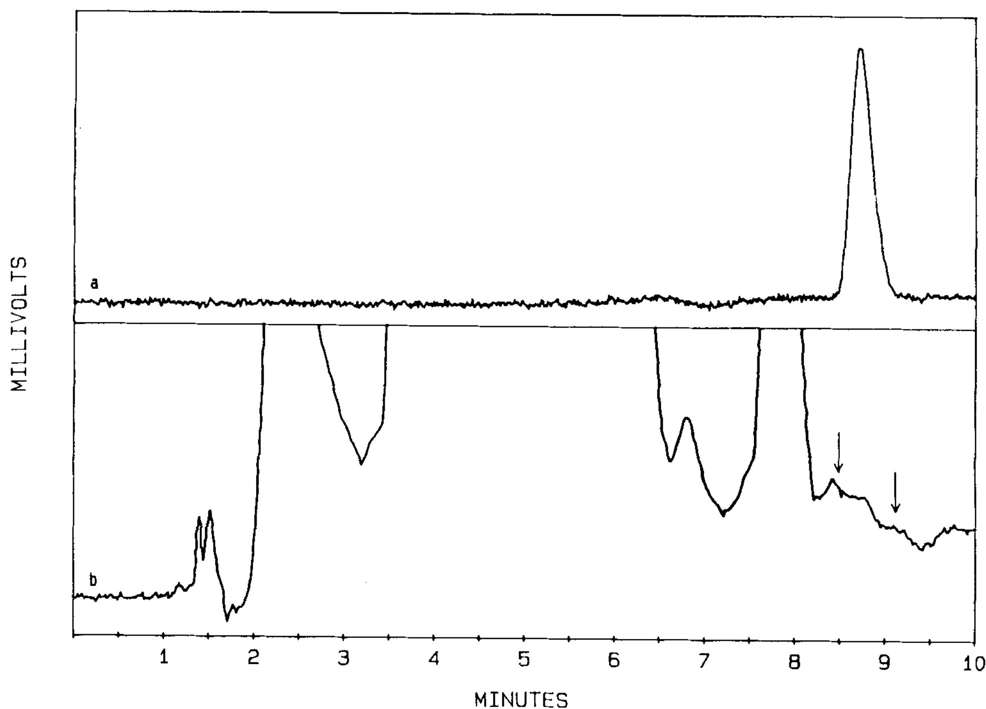

FIGURE 2. HPLC analyses using only the first analytical column. Chromatogram a: linuron standard; chromatogram b: saskatoon berry check sample.

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same mobile phase (40% aqueous methanol) in both analytical columns would not permit any peak compression when the linuron peak was transferred to the second column. However, the column switching produced little or no effect on the resolution of the linuron peak and this was probably due to the higher efficency of the 4 μ particle size of the second analytical column. For maximum sensitivity, detection was made at 248 nm since the stop flow spectrum resulting from a spectral scan of a linuron standard indicated an absorbance maximum at this wavelength.

Analysis of the saskatoon berry check extracts using only the first analytical column produced chromatograms such as that

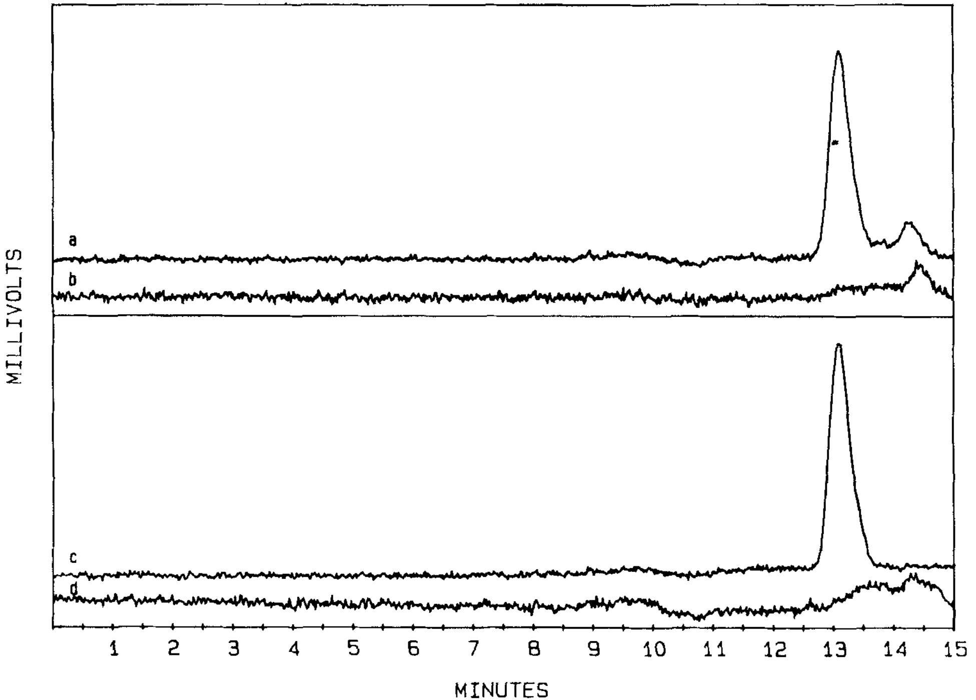

FIGURE 3. HPLC analyses with column switching. Chromatogram a: saskatoon berries fortified at 50 μg/kg; chromatogram b: treated saskatoon berry sample; chromatogram c: linuron standard (25 ng) equivalent to 50 μg/kg; chromatogram d: saskatoon berry check sample.

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illustrated by chromatogram b, Figure 2. Transferring to the second analytical column that segment which corresponded to the width of the linuron peak at baseline (8.2 to 9.1 min), resulted in a chromatogram from the second column which had little or no background interference at the retention (13.2 min) for linuron (chromatogram d, Figure 3). The retention time for linuron was very reproducible and this may reflect the fact that the second analytical column remains very clean since very little saskatoon berry coextractives were transferred to the second column. Background interferences at the retention time for linuron did not

vary significantly with either variety or colour of the saskatoon berries analyzed. Of the 20 check samples analyzed, the maximum interference observed was 0.6 µg/kg with the majority of the samples showing no interference. This level of background interference readily permitted a limit of quantification of 10 µg/kg. Recoveries of linuron from saskatoons fortified at the 100, 50 and 10 µg/kg levels were 90.3 ± 4.0%, 86.0 ± 5.9% and 86.0 ± 11.0%, respectively.

Although linuron residues from early spring applications at 4.4 kg/ha would persist in prairie soils (9) until well past the time when the saskatoon berries had ripened, no linuron residues were observed at the limit of quantification (10 µg/kg) of the analytical method in any of the treated berries from any of the four locations. Chromatograms from treated saskatoon berry samples were not significantly different from those observed for check samples. This was not unexpected since, under dryland conditions, linuron would not be readily leached into the root zone of the saskatoon bushes during the interval separating linuron treatment and berry harvest (9), and uptake by the roots and subsequent translocation to the developing berries would not be possible. Only one location was irrigated (Brooks, Alberta) and two irrigations of 2.5 cm each were applied prior to the harvest of the berries in mid July. Although some leaching into the root zone may have occurred (10), no uptake by the roots and subsequent translocation to the berries was evident. The fact that no linuron residues were observed in the ripened berries also suggests that linuron which came in contact with above-ground basal parts of the saskatoon bushes during spraying either was not taken up or, if taken up, was readily metabolized or not translocated to the developing fruit.

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