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Thermospray ionization liquid chromatography–mass spectrometry and chemical ionization gas chromatography–mass spectrometry of hexazinone metabolites in soil and vegetation extracts

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Abstract

We have used thermospray LC–MS to confirm three highly polar metabolites (A, B, and G) of the herbicide hexazinone [3-cyclohexyl-6-(dimethylamino)-1-methyl-1,3,5-triazine-2,4(1H,3H)-dione], and chemical ionization GC–MS to confirm two other metabolites (D and E) in extracts of soil and vegetation from a forest in the Central Alabama Piedmont. Selected-ion monitoring (SIM) of the protonated molecular ions of metabolite A [3-(4-hydroxycyclohexyl)-6-(dimethylamino)-1-methyl-1,3,5-triazine-2,4(1H,3H)-dione] at mass-to-charge ratio (m/z) 269 and metabolite B [3-cyclohexyl-6-(methylamino)-1-methyl-1,3,5-triazine-2,4(1H,3H)-dione] at m/z 239 gave matrix detection limits (MDLs) of 25 ppb (ng/g) and 50 ppb, respectively, in 10 g vegetation samples. MS quantitation for A and B generally confirmed high-performance liquid chromatography data. SIM of the protonated molecular ion of metabolite G [3-cyclohexyl-6-(methylamino)-1,3,5-triazine-2,4(1H,3H)-dione] at m/z 225 afforded an MDL of 5 ppb in 50 g topsoil samples. Metabolite G was not confirmed above the MDL in any of the soils tested. Chemical ionization GC–MS using methane reagent gas gave strong ion signals for metabolite D [3-cyclohexyl-1-methyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione] at m/z 226 and 144 and metabolite E [3-(4-hydroxycyclohexyl)-1-methyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione] at m/z 242, 224, and 144. SIM at these masses afforded MDLs of 50 ppb for D and 400 ppb for E in 10 g vegetation samples.

1. Introduction

The herbicide hexazinone [3 - cyclohexyl - 6 - (dimethylamino) - 1-methyl - 1,3,5 - triazine - 2,4(1H,3H) - dione], marketed by E.I. DuPont de Nemours and Co., under the trade name of Velpar®, is widely used for pine growth release in the Southeastern United States. We recently completed an environmental fate study in the Central Alabama Piedmont in support of reregistration of hexazinone for forestry use in accordance with regulations set forth by the United States Environmental Protection Agency under the Federal Insecticide, Fungicide and Rodenticide Act (40CFR, Part 158.540). Samples from this study were analyzed for ppb (ng/g) levels of the applied herbicide and for all major known metabolites of the parent compound in those

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matrices where previous work [1–4] had shown them to occur. All vegetation samples were analyzed for hexazinone and metabolites A [3 - (4 - hydroxycyclohexyl) - 6 - (dimethylamino) - 1 - methyl - 1,3,5 - triazine - 2,4(1H,3H)dione], B [3 - cyclohexyl - 6 - (methylamino) - 1 - methyl - 1,3,5 - triazine - 2,4(1H,3H)dione], C [3 - (4 - hydroxycyclohexyl) - 6 - (methylamino) - 1 - methyl - 1,3,5 - triazine - 2,4(1H,3H)dione], D [3 - cyclohexyl - 1 - methyl - 1,3,5 - triazine - 2,4,6(1H,3H,5H)trione], and E [3 - (4 - hydroxycyclohexyl) - 1 - methyl - 1,3,5 - triazine - 2,4,6(1H,3H,5H)trione]. All soil samples were analyzed for the above and for metabolite G [3-cyclohexyl - 6 - (methylamino) - 1,3,5 - triazine - 2,4(1H,3H)dione], a suspected soil metabolite [5]. The structures of these compounds are shown in Fig. 1.

Our initial analytical challenge was to develop a rugged chromatographic separation giving baseline resolution of all seven analytes. The published method of Holt [6] used packed-column GC coupled with a nitrogen–phosphorus detector, required derivatization with trifluoroacetic anhydride (TFAA), and did not include metabolite G. Attempts to adapt this procedure to capillary GC conditions revealed the production of complex mixtures of products which had not been observed on packed-column GC, possibly due to irreversible adsorption of the partially derivatized byproducts by active sites on the stationary support.

Isocratic reversed-phase HPLC methods have been reported for the analysis of residues of the parent hexazinone in water [7–10], soil [8–10], and plant tissue [10,11], but in these studies no

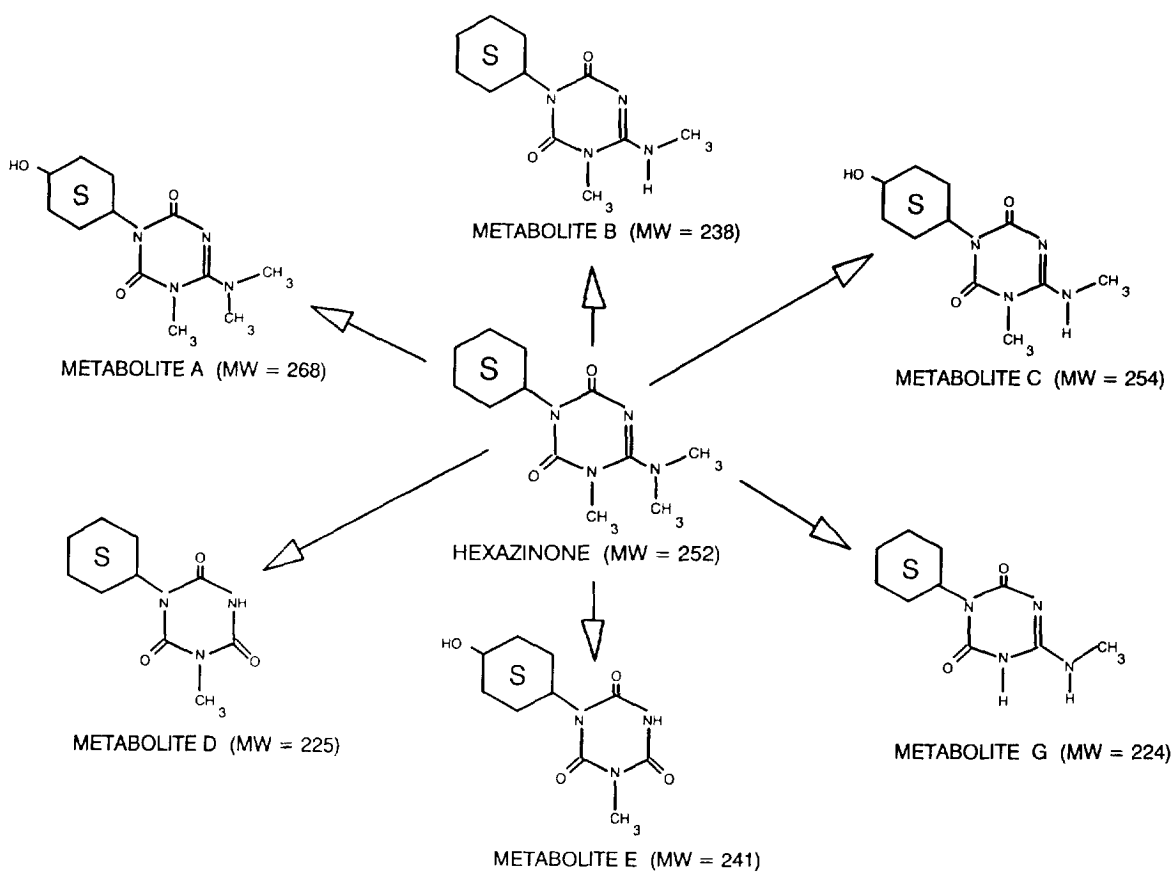

Fig. 1. Hexazinone and its primary soil and vegetation metabolites A through E and G.

attempt was made to simultaneously quantify any metabolites. Earlier work in our laboratory revealed that the range of polarities encompassed by these metabolites is too broad for isocratic elution and that their UV absorbance maxima differ too much for all of them to be detected efficiently at a single wavelength [12]. We therefore developed a reversed-phase gradient elution HPLC separation with time-programmed variable-wavelength UV absorbance detection. A typical chromatogram of a standard mixture of 100 ng each of hexazinone and metabolites A through E and G is shown in Fig. 2. The highly polar 4-hydroxylated cyclohexyl metabolites C, E, and A elute first, followed by the doubly-demethylated metabolite G, then by the singly-demethylated metabolite B, the parent compound, and finally the deaminated metabolite D, which exists almost entirely as the keto-tautomer (i.e., the 1,3,5-trione).

This gradient reversed-phase HPLC separation with programmed variable-wavelength UV absorbance detection, when used in conjunction with a cleanup of the soil and vegetation extracts by treatment with divalent lead [14], was adequate to permit reliable quantitation of most of the analyte components in both matrices.

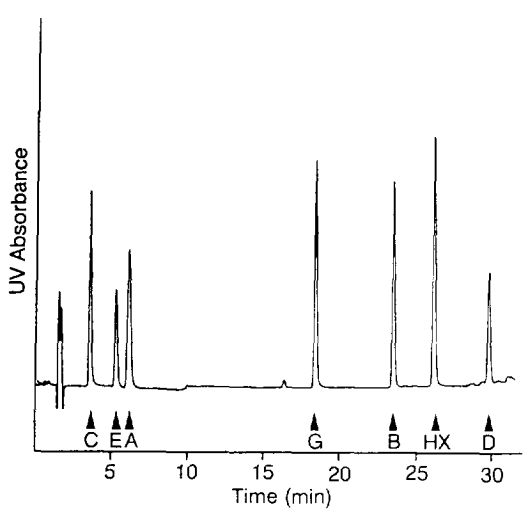

Fig. 2. Gradient HPLC separation of hexazinone and its metabolites with programmed variable-wavelength ultraviolet absorbance detection (chromatographic conditions given in text).

Some uncertainties remained, particularly regarding sporadic high results for metabolite G, which did not correlate with levels of the other analytes and which occurred mainly in surface soil extracts from mid- and toe-slope positions on the Velpar ULW-treated watershed.

Characterization of hexazinone and metabolites A, B, C, D, and E by electron-impact (EI) MS was reported by Reiser et al. [13], but no data was reported for metabolite G. The mass spectra reported were obtained by direct probe or by packed-column GC at the microgram level–lower levels being undetectable except by derivatization with TFAA. Preliminary studies in our laboratory using capillary GC–EI-MS with splitless injection confirmed poor sensitivity for all underivatized metabolites except G, which was not detectable in any amount, even by SIM.

In an effort to avoid derivatization and utilize the power of the reversed-phase HPLC separation already developed, we investigated thermospray ionization as an alternative interface technique for MS confirmation of hexazinone metabolites in soil and vegetation samples. We report on the initial development of thermospray LC confirmation methods for metabolite G in soil samples and for metabolites A and B in forest vegetation samples, as well as their application to actual environmental residue samples from our field study. We also report on the development of a chemical ionization (CI) GC–MS method for the confirmation of metabolites D and E in forest vegetation samples, and the results of its application to the samples from our field study.

2. Experimental

2.1. Materials and methods

Gradient HPLC components

LDC CM4000 multiple solvent delivery system and SM4000 programmable variable-wavelength absorbance detector (LDC Analytical, Riviera Beach, FL, USA), WISP 710B autoinjector (Waters Chromatography Div., Millipore Corp., Milford, MA, USA), Shimadzu CTO-6A column

oven (Shimadzu Scientific Instruments, Columbia, MD, USA), Spectra-Physics SP4400 Chrom-Jet integrator (Spectra-Physics Analytical, Fremont, CA, USA), and Beckman Ultrasphere ODS 150 cm × 4.6 mm I.D. column (Beckman Instruments, San Ramon, CA, USA).

HPLC mobile phases

Solutions: (A) acetonitrile–water (8.5:91.5, v/v); (B) acetonitrile–water (30:70, v/v); (C) acetonitrile–water (70:30, v/v). Gradient: 100% A (0–4 min); 100% A to 100% B (4–26 min); 100% B to 100% C (28–29 min); flush with 100% C (29–38 min); 100% C to 100% A (38–39 min); reequilibrate with 100% A (39–50 min). Total flow-rate, 1.0 ml/min; column temperature, 40°C.

HPLC ultraviolet absorbance detection wavelength program

Wavelengths: 230 nm (0–4.5 min) for metabolite C; 200 nm (4.5–10 min) for metabolites E and A; 230 nm (10–25 min) for metabolites G and B; 245 nm (25–28.5 min) for hexazinone; 200 nm (28.5–33 min) for metabolite D; 0.01 AUFS; plot speed, 0.5 cm/min.

Mass spectrometer

Finnigan MAT 4510B quadrupole mass spectrometer with 9611 gas chromatograph, pulsed positive-ion/negative-ion chemical ionization option, SuperIncos data system, and Finnigan thermospray LC interface. Vaporizer tube fitted with laser-drilled sapphire spray tip (0.0025 inch I.D.).

LC components

Waters M6000A solvent pump with pulse dampener, Rheodyne 7125 loop injector with 20-μl loop, Beckman Ultrasphere-ODS guard column (4.5 cm × 4.6 mm I.D.).

Mobile phases

Metabolite G: methanol–water (30:70, v/v) (0.05 *M* ammonium acetate) pumped at 1.0 ml/min at room temperature (21°C); back pressure 1600–1800 psi.

Metabolites A and B: acetonitrile–water (15:85, v/v) (0.05 *M* ammonium acetate) pumped at 1.0 ml/min at room temperature (21°C); back pressure 1300–1500 psi.

Thermospray operating conditions

Ion source block, 230°C; vaporizer tube, 90°C; aerosol spray, 264°C; repeller electrode, +30 V; filament off.

MS acquisition parameters

Full scan; mass range 120–300; 0.95 s/scan + 0.05 s bottom settling time; 600 scans/run (10.0 min).

SIM, metabolite G; total scan time, 1.000 s; mass interval 224.567–225.567 acquire 0.839 s; 600 scans/run (10.0 min).

SIM, metabolites A and B; total scan time, 1.000 s; mass intervals 238.572–239.572 acquire 0.419 s, 268.580–269.580 acquire 0.426 s; 600 scans/run (10.0 min).

Gas chromatographic conditions for metabolites D and E

Finnigan 9611 gas chromatograph with heated pass-through capillary MS interface; J&W fused-silica capillary column, 14 m × 0.25 mm I.D., 0.25 μm SE-54 film (J&W Scientific, Folsom, CA, USA); carrier gas, helium at 3.5 psi head pressure, 53 cm/s at 120°C; 1 μl splitless injection at 120°C, purge on at 0.7 min; oven temperature 120°C (1.0 min) to 250°C at 20°C/min, hold to 10.0 min; transfer oven temperature, 250°C; manifold temperature, 90°C.

GC–CI-MS acquisition parameters

Electron energy, 110 eV; ion source temperature, 150°C; source pressure, 1.0 mm Hg.

Full scan; mass range 100–300, 0.95 s/scan + 0.05 s bottom settling time; 500 scans/run (8.33 min).

SIM, metabolites D and E; total scan time 1.000 s, scanning mass intervals 143.543–144.543 (acquire 0.213 s), 223.567–224.567 (acquire 0.210 s), 225.568–226.568 (acquire 0.213 s), and 241.572–242.572 (acquire 0.210 s); 500 scans/run (8.33 min).

Analytical standards

Hexazinone metabolites A (Lot no. T3937-2, 98.4%), B (Lot no. A3928-4, 98.8%), D (Lot no. B2838-6, 99.97%), E (Lot no.T3936-3, 99.9%), and G (Lot no. T4916-2, 99.1%) all supplied courtesy of E.I. DuPont de Nemours and Co. (Wilmington, DE, USA).

Solvents

Acetonitrile, chloroform, methanol, and HPLC grade water (Burdick and Jackson Div., Baxter Diagnostics, Muskegon, MI, USA).

Reagents

Ammonium acetate, 99+% (Aldrich Chemical Co., Milwaukee, WI, USA) stored in a desiccator over anhydrous calcium sulfate (Drierite, W.A. Hammond Co., Xenia, OH, USA) until ready for use; anhydrous powdered sodium sulfate and granular lead(II) acetate trihydrate (J.T. Baker, Phillipsburg, NJ, USA).

Solid-phase extraction (SPE) columns

Bakerbond SPE no. 7189-07 light load octadecyl (C_{18}), 6-ml HC, Lot no. E13502, packed with 1000 mg reversed-phase octadecylsilane bonded to silica gel (40 μm APD, 60 Å) (J.T. Baker, Phillipsburg, NJ, USA).

2.2. Sample preparation, determination and quantitation

One watershed of 76 hectares (ha) was treated with the liquid formulation Velpar-L at 6 kg active ingredient per hectare (ai/ha). An adjacent watershed of 75 ha was treated with the pellet formulation Velpar-ULW at 6 kg ai/ha. A third watershed (96 ha) was left untreated as a control. Over 1200 soil core samples, and 600 vegetation samples from each of 4 species (blueberry, bracken fern, dogwood, and bunchgrass) were collected from a gridwork of sites throughout these three adjacent watersheds during the 12-month period following application. Soil samples (50 g) were dried, pulverized, extracted with 3–68 ml portions of methanol–water (4:1), evaporated, treated with 2 ml of 1 *M* lead(II) acetate, filtered through GF/B glass fibre paper, concentrated on 1000 mg C_{18} SPE columns, and eluted with methanol. Vegetation samples (10 g) were pulverized with dry ice, dried by blending intimately with 20 g of anhydrous powdered sodium sulfate, extracted with 3–68 ml portions of chloroform, filtered through GF/B glass fibre paper, rotoevaporated into water, treated with 2 ml of 1 *M* lead(II) acetate, filtered through GF/B paper, concentrated on C_{18} SPE columns, and eluted with methanol [14].

Every sample extract injected into the mass spectrometer was compared to a set of external standards of the analyte(s) of interest run the same day. These standards were made up in methanol at concentrations spanning the range from the detection limit to the highest anticipated sample level. Typical calibration standard levels for thermospray analyses of metabolite G in soil samples were 0.5, 2, 5, 20, and 50 ng/g. Typical calibration levels for thermospray analyses of metabolites A and B in vegetation were 1, 10, 100, 200, and 400 ng/g. Typical calibration levels for GC–CI-MS analyses of metabolites D and E in vegetation were 0.5, 1, 2, 5, 10, 20, 50, and 100 ng/g. A full calibration curve was run at the beginning of each day, followed by random single standards after every 4 samples. Minimum matrix detection levels (MDLs) were estimated based on a peak height of three times the background noise level. Responses were nonlinear, especially for CI of metabolites D and E. Calculations assumed quantitative recovery in the extracts.

3. Results and discussion

3.1. Metabolite G in soil samples

Metabolite G has been identified as a potential metabolite of hexazinone in soil [5], but there are no published chromatographic or mass spectral data. A typical HPLC–UV chromatogram of a soil extract appearing to contain metabolite G is shown in Fig. 3. Close examination of many such chromatograms revealed that the retention time of the "G" peak was always 0.1–0.2 min

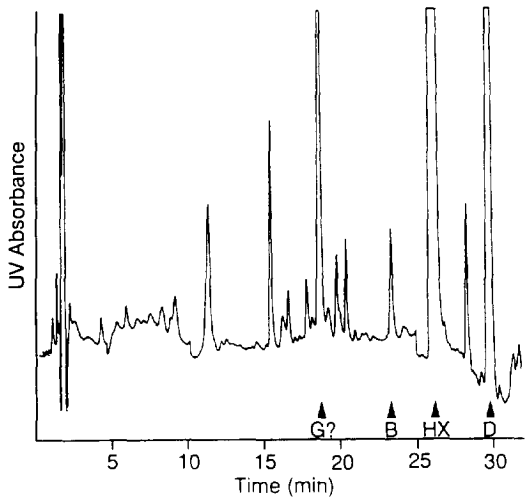

Fig. 3. Extract of hexazinone-treated surface soil. Same chromatographic conditions as Fig. 2.

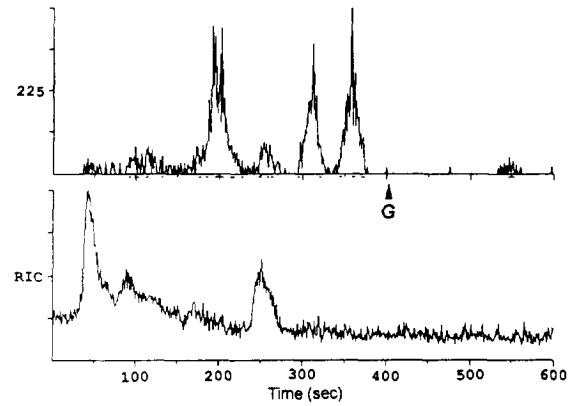

Fig. 4. Full scan thermospray ion chromatogram (1.0 s/scan) of surface soil extract (10-μl injection). Lower trace full scan (mass range 120–300); upper trace single-ion chromatogram (m/z 225). Chromatographic conditions given in Experimental section.

later than that of metabolite G standards chromatographed before and after the sample extract. Reanalysis of some of these samples with detection at a different UV wavelength (200 nm vs. 230 nm) produced a ratio of absorbances (A_{200}/A_{230}) that was about 1.2 as opposed to 2.9 for an authentic metabolite G standard. These facts led to questioning the authenticity of the "G" peak in these soil extracts and called for identity confirmation by an independent technique. As noted above, metabolite G cannot be analyzed by GC–MS without derivatization. It chromatographs well, however, under reversed-phase HPLC conditions, making it a natural candidate for thermospray LC–MS. Under thermospray conditions with a vaporizer tube temperature of 90°C and a repeller voltage of +30 V, metabolite G produces only one ionic species, the protonated molecule at m/z 225. The high noise and low sensitivity characteristic of full scan thermospray operation can be largely eliminated by SIM at m/z 225 only. Metabolite G is insoluble in water and soluble in methanol at room temperature (1 mg/ml), partially reprecipitating at 4°C. Its tendency to reprecipitate may account for the pronounced tailing under thermospray conditions using methanol–water (30:70) (0.05 M NH_4OAc). Less tailing is evident using acetonitrile–water, but interferences appear in soil extracts at m/z 225 which do not occur with methanol–water. A typical full scan thermospray chromatogram of a surface soil extract is shown in Fig. 4 together with the selected-ion scan at m/z 225. No trace of metabolite G is seen at its retention time of 405 s (6.75 min), even though the original HPLC chromatogram (Fig. 3) showed a 630 ppb peak. A rechromatograph of this sample under SIM conditions confirmed that metabolite G is not present above the MDL of 5 ppb. Nearly 200 soil samples that had shown levels of metabolite G greater than 20 ppb under gradient HPLC conditions were reanalyzed using thermospray LC–MS with SIM at 225 m/z. Metabolite G was not detected above the MDL of 5 ppb in any of these samples, even though QC soil samples spiked at 50 ppb consistently gave 60% recoveries. Thus we have not been able to confirm its natural occurrence as a metabolite of hexazinone in soil.

3.2. Metabolites A and B in vegetation samples

Metabolites A and B are the primary metabolites of hexazinone, resulting from hydroxylation (A) or demethylation (B) of the parent compound. They are the easiest of the metabolites to analyze as they can be gas chromatographed without derivatization. Using modifications of the Holt procedure, J.C. Feng and co-workers [15–20] have reported levels of A and B in

Canadian soil and vegetation [20] which track residual hexazinone levels fairly closely. Metabolite B is consistently the most abundant metabolite. We were able to reliably quantify A and B in our soil extracts using gradient HPLC, but vegetation extracts often contained high levels of coextracted coeluting interferences. Metabolites A and B differ greatly in polarity, but can be chromatographed isocratically with an acetonitrile–water (15:85, v/v) (0.05 *M* NH_4OAc) mobile phase. At a vaporizer tube temperature of 90°C and a repeller voltage of +30 V, metabolites A and B, like G, exhibit no decomposition and produce only their protonated molecules at *m/z* 269 for A and *m/z* 239 for B (Fig. 5). SIM at only these two masses affords MDLs of 25 ppb for A and 50 ppb for B. A full scan thermospray LC–MS chromatogram of a typical grass extract is shown in Fig. 6. Calculated levels of metabolites A and B in this sample by HPLC with UV absorbance detection were 4.1 ppm (mg/g) and 14.5 ppm, respectively. Reanalysis of this sample by thermospray-SIM confirmed the presence of both metabolites at roughly these levels. Almost 60 vegetation samples showing high levels of A and/or B on gradient HPLC were reanalyzed by thermospray LC–MS. Quantitation by LC–MS generally confirmed levels quantitated by gradient HPLC. In all cases the presence of metabolite B was confirmed. The presence of metabolite A was confirmed in all samples but two.

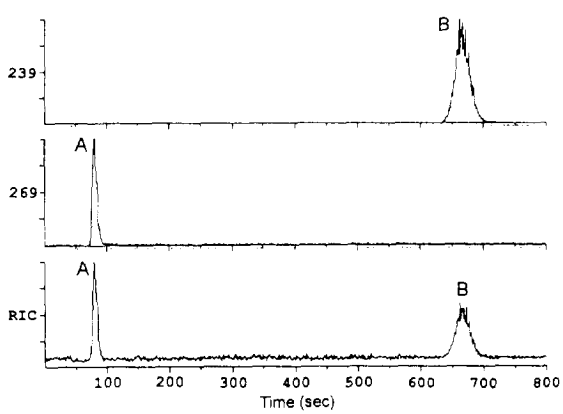

Fig. 5. Full scan thermospray total-ion chromatogram (1.0 s/scan) of a mixed standard of 200 ng each metabolites A and B (conditions given in text). Lower trace full scan (mass range 120–300); middle trace single-ion chromatogram of A (*m/z* 269); upper trace single-ion chromatogram of B (*m/z* 239).

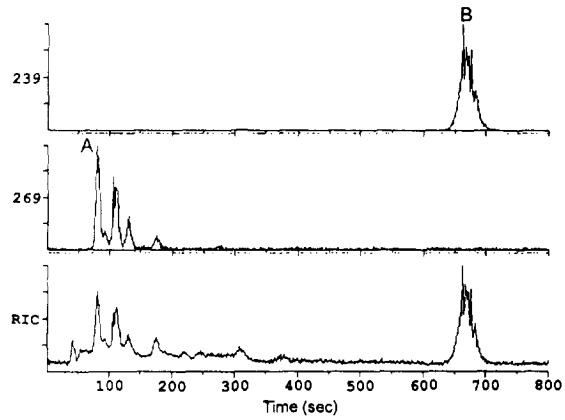

Fig. 6. Full scan thermospray total-ion chromatogram of grass extract with single-ion traces at *m/z* 269 (metabolite A) and *m/z* 239 (metabolite B). All conditions same as Fig. 5.

3.3. Metabolites D and E in vegetation samples

The two deaminated metabolites D and E are exceptionally difficult to detect selectively due to their highly stable 1,3,5-triazine-2,4,6-trione ring structures. Their UV absorbance maxima lie below 200 nm, necessitating detection at this unselective wavelength where many plant coextractives absorb strongly. This places heavy demands on sample cleanup procedures and virtually guarantees coeluting interferences from one or more plant species. Their stable ring structures also make D and E unresponsive to the NPD rubidium bead nitrogen-selective GC detector. We found that D and E exhibit no response to thermospray LC–MS, presumably due to their failure to form association complexes with protons or ammonium ions in aqueous solution. Metabolites D and E can be analyzed by capillary GC–MS but we found that they exhibit very low sensitivities under EI conditions. Neither compound gives a detectable molecular ion. The base peak in both cases is the resonance-stabilized double hydrogen rearrangement ion at *m/z* 144, which was described by Reiser et al. [13]. Full scan EI–MS of splitless

1-μl injections gives on-column detection limits of 10 ng for D and 25 ng for E, corresponding to MDLs of 5000 ppb and 12 500 ppb, respectively, in 10 g vegetation samples–too high for confirmation purposes. SIM at *m/z* 144 only improves the MDLs to 1000 ppb and 5000 ppb, respectively. We therefore investigated CI as an alternative ionization mode for metabolites D and E because the high ion source pressures and confinement times of CI should greatly increase the probability of ion-yielding collisions. Full scan CI using methane reagent gas at a source pressure of 1.0 mm Hg gave two major ions for metabolite D, the protonated molecule at *m/z* 226 and the *m/z* 144 rearrangement ion (see Table 1). CI of metabolite E gave the protonated molecule at *m/z* 242, the base peak at *m/z* 224 $[242 - H_2O]^+$, and the *m/z* 144 rearrangement ion. SIM at masses 144, 224, 226, and 242 afforded MDLs of 50 ppb for D and 400 ppb for E, just adequate for confirmation.

GC–MS-CI-SIM was applied to 56 vegetation samples that had shown high levels of metabolites D and/or E. Fig. 7 shows a typical gradient HPLC chromatogram of a suspect vegetation sample, which exhibited 18.3 ppm of metabolite D and 1.5 ppm of metabolite E. Fig. 8 shows the corresponding CI-SIM chromatogram of this sample, which confirms the presence of both metabolites. Metabolite D was confirmed in all vegetation samples tested, although usually at a lower concentration than observed with HPLC, suggesting the presence of coeluting interferences absorbing at the UV detection wavelength of 200 nm. Metabolite E was confirmed in 23 of the 56 samples tested.

Table 1
Chemical ionization positive-ion mass spectra of hexazinone metabolites D and E

Compound	*m/z*	Relative abundance	Assignment
Metabolite D	226	100	$[M + H]^+$
	144	25	Rearrangement
Metabolite E	242	36	$[M + H]^+$
	224	100	$[M + H - H_2O]^+$
	144	30	Rearrangement

Conditions: methane reagent gas at source pressure 1.0 mm Hg. Filament ionization at 110 eV. Full scan *m/z* 100–300 at 1.0 s/scan.

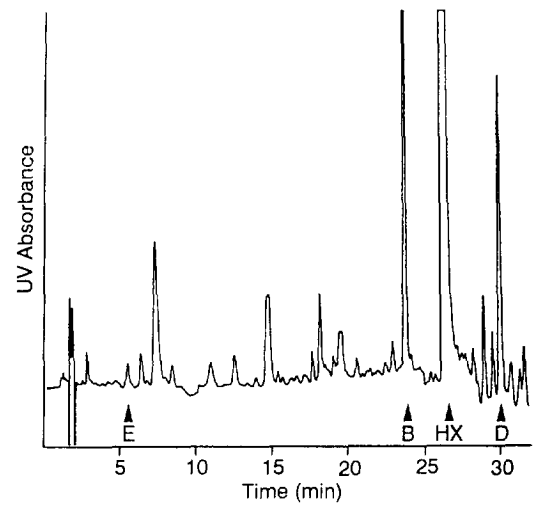

Fig. 7. Gradient HPLC chromatogram of an extract of blueberry leaves and branches from a hexazinone-treated site. Chromatographic conditions same as Fig. 2.

4. Conclusions

We have developed selective, sensitive, and reliable thermospray LC–MS methods for identi-

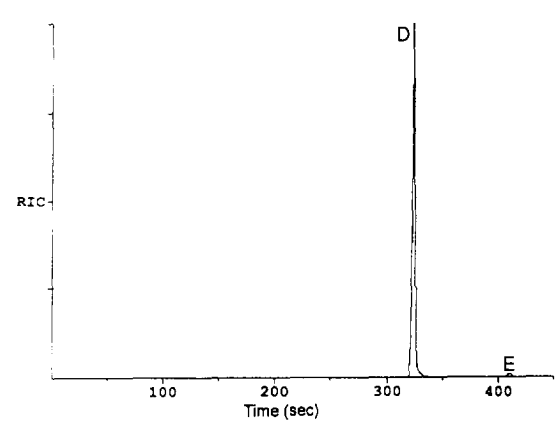

Fig. 8. GC–CI-SIM chromatogram of a 1-μl splitless injection of the same blueberry extract as in Fig. 7. Temperature-programmed GC conditions given in text. Methane reagent gas (1.0 mm Hg) with filament ionization at 110 eV. Acquisition at *m/z* 144, 224, 226, and 242 (0.21 s each; 1 s/scan).

ty confirmation of three highly polar metabolites of hexazinone (A, B, and G) in samples of forest soil and vegetation from the Southeastern United States. Metabolites A and B were confirmed in four plant species using thermospray LC–MS-SIM at m/z 269 and 239, respectively. MDLs of 25 ppb for A and 50 ppb for B were achieved in 10 g vegetation samples.

Thermospray LC mass spectra are presented for the first time for metabolite G, a suspected metabolite of hexazinone in soil. Soil samples were identified by HPLC with UV detection to contain metabolite G at concentrations above 20 ppb, but when these samples were reanalyzed by thermospray LC–MS-SIM at m/z 225 metabolite G was not detected above an MDL of 5 ppb. Therefore, we were unable to confirm the existence of metabolite G in soil. Metabolites D and E, which have resisted detection by other means including thermospray LC–MS, were confirmed in vegetation samples by GC–MS-CI-SIM at m/z 144, 224, 226, and 242 with MDLs of 50 and 400 ppb respectively. No derivatization was required for any of these procedures.

While thermospray LC–MS has been eclipsed by newer techniques, such as electrospray and atmospheric pressure ionization, we have found thermospray to be a rugged, sensitive, and selective technique for the confirmation of polar and/or thermally-labile small molecules, like herbicide metabolites, in extracts of complex environmental matrices, especially when used in the selected-ion monitoring mode.

Acknowledgements

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