tested for bitertanol sensitivity varied with the crop due to tolerance data. Samples of apples, watermelons, mangoes, peaches, guavas, and beans were fortified with bitertanol in the 0.1–0.6 ppm range. Figure 4 illustrates typical gas chromatograms of samples fortified at 0.6 ppm (watermelons), 0.5 ppm (peaches), and 0.1 ppm (apples). Table I shows the recovery of bitertanol as the acetylated bitertanol in fortified samples.

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# Gas Chromatography–Mass Spectrometry of Acylalanine Fungicides

Brian D. Ripley

Gas chromatographic–mass spectral data are presented for nine parent acylalanine fungicides and twelve metabolites or derivatives. Most compounds show similar fragmentation patterns indicating numerous single bond cleavages. For methoxyacetyl congeners, the base peak is usually $m/z$ 45. The benzyl alcohol atropisomers of metalaxyl undergo thermal rearrangement in the gas chromatograph with loss of $CH_3OH$ to produce a lactone that fragments with a base peak of $m/z$ 146. All compounds have unique retention times on a SE-30 capillary column and common ions for most of the parent fungicides and their metabolites allow multiple-ion monitoring for confirmation.

The acylalanine fungicides are quickly becoming important in crop protection due to their systemic properties with both curative and protective activity against fungal pathogens of the Peronosporales. The general structure of the acylalanines is shown in Figure 1.

These compounds are structurally similar to the chloroacetamide (or acylanilide) herbicides such as alachlor and metolachlor. The term acylalanine was used by Ciba-Geigy (Staub et al., 1978) to describe their chemicals that had $R_1$ = alanine methyl ester but has become commonplace for all systemic fungicides of this general structure that are active against Oomycetes. Gisi and Wiedmer (1983) described these chemicals as phenylamides of three chemical subclasses differing in the $R_1$ substituent: the acylalanines (metalaxyl, furalaxyl, benalaxyl), the butyrolactones (ofurace, cyprofuram), and oxazolidinones (oxadixyl). The $R_2$ substituents include methoxymethyl, chloromethyl, as well as numerous other acyl derivatives. All the acylalanines described in this paper (Table I) are 2,6-dimethylaniline derivatives except cyprofuram which is a 3-chloroaniline derivative. Structure–activity relationships based on physicochemical properties have been discussed by Hubele et al. (1983).

This study was undertaken to obtain gas chromatographic-mass spectra of the parent fungicides, their metabolites, and derivatives, and to elucidate fragmentation patterns so that subsequent metabolic and residue studies could be conducted with MS confirmation or single- or multiple-ion quantitation.

## EXPERIMENTAL SECTION

Gas chromatography–mass spectrometry (GC–MS) was conducted on a Hewlett-Packard 5970 mass selective detector (MSD). A Hewlett-Packard 5790 gas chromatograph with a 15 m × 0.25 mm fused silica capillary column with a 0.25-$\mu$m coating of SE-54 and He carrier gas flow of 2 mL min$^{-1}$ was connected to the MSD with a direct capillary interface operated at 260 °C. One-microliter solutions were injected with a splitless injector operated at 220–250 °C with the bypass valve open for 1 min. The column oven was programmed for an initial 1-min hold at 90 °C, followed by a 10 °C min$^{-1}$ rise to 270 °C and a final hold at this temperature to allow elution of late compounds.

The MSD was optimized by using Hewlett-Packard disk software under AUTOTUNE conditions with PFTBA (perfluorotributylamine) calibration. Mass spectra were acquired over the 40–400 amu range at 380 amu s$^{-1}$ and normalized to DFTPP (decafluorotriphenylphosphine). Single- or multiple-ion monitoring was conducted with Hewlett-Packard software with up to 20 ions being monitored.

Retention time data were generated on a Hewlett-Packard 5880 capillary gas chromatograph with a 15 m × 0.25 mm fused silica capillary column with a 0.25-$\mu$m coating of SE-30 under the conditions described by Ripley and Braun (1983).

Parent acylalanines were analytical or technical grade and were prepared at 1 mg mL$^{-1}$ in methanol and appropriately diluted to obtain 10 or 100 $\mu$g mL$^{-1}$ solutions for GC–MS. Metabolites or derivatives were supplied by Ciba-Giegy (CGA) or synthesized by using standard procedures.

## RESULTS AND DISCUSSION

The mass spectra of metalaxyl (Marucchini et al., 1983; Ripley, 1984) and ofurace (Cooke et al., 1982) have been reported previously and tentative fragmentation patterns have been made (Cooke et al., 1982; Ripley, 1984). This study confirms that all the examined acylalanines, their metabolites, and derivatives follow this general pattern as shown in Figure 2. The acylalanine compounds exhibit

Provincial Pesticide Residue Testing Laboratory, Agricultural Laboratory Services, Ontario Ministry of Agriculture and Food, University of Guelph, Guelph, Ontario N1G 2W1 Canada.

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**Table I. Common, Chemical, and Trade Names of the Acylalanine Fungicides**

| common name[a] (code number) | chemical name[b] | code number, trade name |
|---|---|---|
| metalaxyl | *N*-(2,6-dimethylphenyl)-*N*-(methoxyacetyl)-DL-alanine methyl ester | Ridomil, Apron, Subdue, CGA-48988 |
| furalaxyl | *N*-(2,6-dimethylphenyl)-*N*-(2-furanylcarbonyl)-DL-alanine methyl ester | Fongarid, CGA 38140 |
| benalaxyl | *N*-(2,6-dimethylphenyl)-*N*-(phenylacetyl)-DL-alanine methyl ester | Galben |
| CGA-29212 | *N*-chloroacetyl-*N*-(2,6-dimethylphenyl)-DL-alanine methyl ester | CGA-29212 |
| ofurace | 2-chloro-*N*-(2,6-dimethylphenyl)-*N*-(tetrahydro-2-oxo-3-furanyl)acetamide | Caltan, Milfuram, RE-20615 |
| RE-26745 | *N*-(2,6-dimethylphenyl)-2-methoxy-*N*-(tetrahydro-2-oxo-3-furanyl)acetamide | RE-26745 |
| RE-26940 | *N*-(2,6-dimethylphenyl)-2-methoxy-*N*-(tetrahydro-2-oxo-3-thienyl)acetamide | RE-26940 |
| oxadixyl | *N*-(2,6-dimethylphenyl)-2-methoxy-*N*-(2-oxo-3-oxazolidinyl)acetamide | SAN 371 |
| cyprofuram | *N*-(3-chlorophenyl)-*N*-(tetrahydro-2-oxo-3-furanyl)cyclopropanecarboxamide | Vinicur |

[a] Proposed or accepted [b] Chemical abstracts.

**Table II. Major Fragmentation Ions and Percent Intensity for the Parent Acylalanine Fungicides**

| compound | $M^+$ | $m/z$ (% intensity)[a] |
|---|---|---|
| metalaxyl | 279 | 279 (1), 249 (6), 234 (7), 220 (11), 206 (23), 192 (13), 174 (6), 162 (9), 160 (21), 148 (10), 146 (18), 132 (18), 130 (17), 105 (10), 91 (4), 77 (8), 59 (10), 45 (100) |
| furalaxyl | 301 | 301 (4), 269 (3), 242 (24), 225 (3), 214 (2), 206 (3), 180 (5), 152 (14), 146 (10), 132 (5), 117 (3), 105 (4), 103 (12), 95 (100), 91 (2), 77 (5) |
| benalaxyl | 325 | 325 (3), 294 (1), 266 (7), 234 (14), 206 (24), 204 (23), 176 (15), 148 (100), 132 (11), 91 (34) |
| oxadixyl | 278 | 278 (4), 250 (4), 233 (17), 219 (5), 205 (2), 163 (70), 146 (12), 133 (21), 132 (47), 131 (15), 120 (29), 119 (12), 118 (11), 105 (51), 91 (12), 79 (14), 77 (17), 45 (100) |
| ofurace | 281 (1 Cl) | 283 (7)/281 (24),[b] 246 (2), 245 (1), 233 (12), 232 (76), 222 (11), 208 (7), 204 (31), 202 (16), 199 (4), 197 (10), 188 (12)/186 (37), 180 (7), 176 (6), 174 (7), 162 (21), 160 (91), 158 (23), 148 (17), 146 (40), 144 (35), 132 (100), 130 (28), 118 (15), 117 (24), 105 (26), 103 (19), 91 (16), 85 (29), 79 (21), 77 (44), 65 (15), 51 (15), 49 (14), 41 (14) |
| RE-26745 | 277 | 277 (9), 247 (6), 245 (4), 232 (36), 204 (24), 188 (6), 186 (20), 176 (8), 160 (20), 156 (16), 146 (19), 144 (23), 132 (30), 130 (15), 119 (11), 117 (11), 105 (20), 91 (8), 79 (11), 77 (19), 45 (100) |
| RE-26940 | 293 | 293 (5), 265 (29), 248 (1), 246 (4), 232 (10), 220 (11), 206 (4) 204 (12), 192 (35), 186 (4), 176 (10), 172 (5), 160 (29), 158 (12), 146 (10), 144 (20), 132 (69), 130 (8), 128 (21), 117 (9), 105 (13), 103 (9), 91 (5), 79 (12), 77 (12), 45 (100) |
| cyprofuram | 279 (1 Cl) | 281 (2)/279 (8),[b] 249 (0.1), 221 (1), 213 (20)/211 (60), 169 (2)/167 (7), 168 (1)/166 (3), 155 (1)/153 (3), 140 (1)/138 (4), 130 (4), 117 (2), 113 (3)/111 (11), 75 (8), 69 (100), 41 (59) |
| CGA-29212 | 283 (1 Cl) | 285 (0.7)/283 (2),[b] 252 (1), 248 (1), 234 (10), 226 (10)/224 (36), 216 (2), 202 (3), 174 (3), 163 (3), 162 (8), 148 (100), 136 (5), 134 (16), 132 (20), 117 (7), 105 (9), 103 (5), 91 (4), 77 (11) |

[a] Percent intensity rounded off. [b] All paired ions show one chlorine pattern.

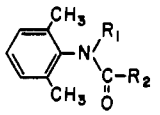

**Figure 1.** General structure of acylalanine fungicides.

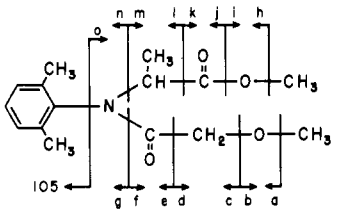

**Figure 2.** General fragmentation pattern for acylalanine fungicides, illustrated for metalaxyl.

weak to moderately intense molecular ions and numerous characteristic ions at moderate intensity were found at even $m/z$ values indicating single bond cleavage.

The base peak in most cases arises from cleavage of d–e or f–g (Figure 2). For example, when the acyl substituent $R_2$ (Figure 1) is methoxymethyl, [M – 73] is a major fragment ion and loss of neutral CO from the substituted acyl fragment or d–e cleavage on the parent molecule results in a base peak of $m/z$ 45; [M – 30] ([M – $OCH_3$] + H) and [M – 45] are also evident. This fragmentation tends to predominate regardless of other substituents (Tables II and III), except for the benzyl alcohol metabolite of metalaxyl. Similarly, f–g cleavage results in the base peak peak of $m/z$ 69 (cyclopropyl carbonyl) in cyprofuram and $m/z$ 95 (furyl carbonyl) in furalaxyl. The base peak for benalaxyl ($m/z$ 148) results from cleavage of both d–e ($m/z$ 91, methylphenyl) and m–n (methyl propionate). CGA-29212 also shows a base peak of $m/z$ 148 due to similar fragmentation. In contrast, ofurace, the related chloroacetamide, has a base peak at $m/z$ 132 due to [Ph-$(CH_3)_2$ – N(CH)] (Cooke et al., 1982). Ofurace alcohol has $m/z$ 232 ([M – $CH_2OH$]) as the base peak but also an intense ion at $m/z$ 132 (92%).

Benzyl alcohol atropisomers of metalaxyl and their derivatives often have $m/z$ 263 as the apparent molecular ion indicating loss of $CH_3OH$ and rearrangement to a single lactone product (Gross, 1979). This is particularly evident at low concentrations and at high injector temperatures indicating thermal decomposition and rearrangement in the gas chromatograph. At lower injector temperatures (220 °C) two peaks are evident on the chromatogram which were identified as the intact benzyl alcohol ($m/z$ 295) and the rearrangement lactone product ($m/z$ 263). Subsequent cleavages appear for loss of $m/z$ 45/73 and 44 ($-CO_2$) to produce the base peak of $m/z$ 146 or 45. Alkyl derivatives of metalaxyl benzyl alcohol also produce intense $m/z$ 45 or 146 ions.

Fragmentation of the $R_1$ groups usually contribute minor ions to the mass spectra. Cleavage of k–l [M – 59] or loss of $COOCH_3$ from other ions predominates. The $R_1$ alkyl substituent on the aniline tends to stabilize the fragment and $m/z$ 132 is common to most of the spectra. When $R_1$ is a ring structure, m–n fragmentation is often absent. The two butyrolactones indicate dissimilar fragmentation because of their respective $R_2$ substituent. Ofurace has an intense ion at $m/z$ 85 and a [M – 85 + H] ion, as well as [M – 59] from the lactone ring opening. Cyprofuram loses $m/z$ 44 from the f–g fragment ion and has a very weak $m/z$ 132 fragment. Oxadixyl indicates fragment ions for loss of $m/z$ 28 and 59. Analogous to $m/z$ 162 in ofurace, oxadixyl has a fragment ion at $m/z$ 163 and cyprofuram has

**Table III. Major Fragmentation Ions and Percent Intensity for Some Metabolites of Metalaxyl**

| compound | $M^+$ | $m/z$ (% intensity)[a] |
|---|---|---|
| metalaxyl acid | 265 | 265 (2), 250 (0.4), 235 (13), 220 (19), 206 (3), 192 (21), 176 (13), 160 (22), 148 (74), 147 (31), 146 (29), 144 (17), 132 (36), 120 (10), 117 (12), 116 (11), 105 (18), 91 (9), 79 (11), 77 (16), 45 (100) |
| metalaxyl acid (ethyl ester) | 293 | 293 (2), 263 (6), 248 (10), 235 (1), 220 (41), 207 (4), 206 (3), 192 (32), 174 (8), 162 (13), 160 (34), 148 (34), 147 (15), 146 (19), 144 (11), 132 (24), 131 (21), 120 (8), 117 (6), 105 (7), 103 (21), 91 (6), 87 (13), 59 (32), 45 (100) |
| 3-OH metalaxyl (CGA-100255) | 295 | 295 (4), 250 (27), 236 (10), 222 (22), 218 (6), 208 (10), 190 (20), 178 (8), 176 (29), 164 (13), 162 (28), 158 (10), 148 (20), 130 (19), 91 (8), 45 (100) |
| 3-OMe metalaxyl | 309 | 309 (6), 264 (31), 250 (9), 236 (29), 232 (9), 222 (15), 204 (37), 192 (13), 190 (27), 178 (18), 176 (38), 162 (31), 158 (18), 147 (10), 130 (31), 105 (12), 91 (13), 45 (100) |
| 3-OEt metalaxyl | 323 | 323 (3), 278 (14), 264 (4), 250 (16), 246 (4), 236 (8), 218 (21), 204 (19), 192 (11), 190 (31), 176 (14), 162 (10), 158 (11), 148 (15), 130 (31), 91 (14), 45 (100) |
| benzyl alcohol[b] (CGA-94689A) | 295 | 295 (0.3), 277 (0.1), 265 (2), 264 (2), 250 (13), 236 (2), 234 (1), 232 (39), 218 (2), 206 (4), 204 (5), 192 (31), 178 (7), 176 (5), 174 (5), 172 (3), 162 (15), 160 (10), 158 (8), 148 (13), 146 (100), 144 (17), 132 (24), 130 (15), 118 (5), 107 (6), 105 (16), 91 (12), 77 (12), 45 (69) |
| benzyl alcohol[b] (CGA-94689B) | 295 | 295 (0.4), 265 (2), 264 (3), 263 (0.2), 250 (9), 236 (3), 234 (2), 232 (44), 222 (15), 206 (7), 204 (4), 192 (37), 178 (7), 176 (3), 174 (4), 172 (3), 162 (11), 160 (10), 158 (6), 146 (100), 144 (13), 132 (21), 130 (16), 118 (5), 107 (6), 105 (14), 91 (10), 77 (8), 45 (52) |
| benzyl alcohol (CGA-94689) (rearrangement lactone product) | 263 | 263 (2), 233 (2), 219 (37), 204 (4), 191 (2), 189 (5), 176 (12), 174 (44) 160 (46), 147 (20), 146 (90), 144 (20), 132 (19), 131 (29), 130 (15), 118 (6), 105 (27), 103 (11), 91 (10), 79 (13), 77 (18), 65 (8), 63 (4), 45 (100) |
| benzyl alcohol (CGA-94689B) (methyl ether) | 309 | 309 (1.3), 279 (2), 278 (3), 264 (8), 250 (8), 236 (12), 232 (68), 218 (8), 206 (6), 205 (8), 204 (24), 192 (6), 190 (16), 178 (6), 176 (10), 172 (11), 162 (6), 160 (12), 158 (16), 153 (6), 148 (6), 146 (100), 144 (22), 132 (15), 131 (17), 130 (12), 122 (4.5), 119 (7), 117 (12), 105 (15), 91 (7), 83 (17), 83 (14), 77 (10), 55 (13), 45 (66), 43 (14) |
| benzyl alcohol (CGA-94689B) (ethyl ether) | 323 | 323 (1.1), 294 (2.2), 292 (1), 278 (6), 264 (6), 262 (3), 250 (5), 236 (4), 232 (74), 220 (6), 218 (11), 206 (13), 204 (21), 190 (29), 176 (10), 174 (9), 172 (9), 162 (11), 160 (13), 158 (20), 148 (13), 146 (100), 144 (24), 132 (14), 131 (17), 130 (11), 120 (5), 117 (7), 111 (6), 105 (15), 97 (16), 91 (9), 79 (5), 77 (9), 65 (5), 59 (8), 55 (15), 45 (64) |
| benzoic acid (CGA-108905) | 309 | 293 (2), 292 (2), 291 (4), 264 (14), 250 (11), 234 (19), 218 (21), 204 (55), 192 (14), 190 (11), 174 (22), 172 (11), 164 (6), 162 (4), 160 (40), 158 (10), 144 (9), 134 (5), 132 (8), 130 (5), 116 (6), 104 (8), 91 (13), 59 (18), 45 (100) |
| benzoic acid (methyl ester) | 323 | 291 (1.3), 264 (4), 250 (5), 234 (10), 218 (11), 204 (26), 190 (8), 174 (14), 160 (32), 144 (7), 132 (8), 130 (6), 91 (8), 59 (19), 45 (100) |
| benzoic acid (ethyl ester) | 337 | 337 (0.1), 305 (2), 278 (3), 265 (6), 234 (10), 218 (35), 204 (7), 190 (8), 176 (13), 174 (15), 160 (49), 144 (8), 132 (9), 130 (8), 91 (10), 73 (12), 59 (56), 45 (100) |
| ofurace alcohol | 263 (no Cl) | 263 (19), 232 (100), 204 (45), 186 (42), 179 (16), 160 (24), 158 (21), 148 (23), 146 (37), 144 (44), 142 (21), 132 (92), 130 (24), 129 (23), 122 (36), 117 (27) 112 (42), 105 (42), 103 (24), 91 (19), 85 (18), 79 (22), 77 (36), 65 (15), 53 (11), 51 (11), 41 (15) |

[a] Percent intensity rounded off. [b] Atropisomers.

a one chlorine pattern at $m/z$ 166/168. The Chevron chemical RE-26940, that has $R_1$ = 3-(2-oxothiophene), loses $m/z$ 28, 47, and 61 from both the molecular ion and other fragment ions. Businelli et al. (1984) reported a lactone ($m/z$ 233) formed during acidic hydrolysis of metalaxyl involving rearrangement of the $R_1$ and $R_2$ groups; this metabolite had major fragment ions for [M − 58] and $m/z$ 105.

Most of the ions for the other simple fragmentations from the molecular or fragment ions are present in the mass spectrum. For example, metalaxyl and its metabolites show ions for M − 30, − 45, − 59, − 73, − 87, − 105, − 117, − 119, − 131, − 133, and − 147. Common ions associated with the dimethylanilino moieties are $m/z$ 91, 105, 117, 130 and/or 132, 146 and/or 148, and 160. A number of other synthesized products having various $R_1$ and/or $R_2$ groups similar to those of the parent acylalanines had similar fragmentations to those indicated in Figure 2. For example, all $R_2$ = $CH_2OCH_3$ derivatives have a base peak of $m/z$ 45 and when $R_2$ = H and $R_1$ = butyrolactone a base peak of $m/z$ 132 was obtained. Despite the large number of common ions in all the examined compounds, the library search algorithm had no problem in correctly identifying the injected standard.

The application of capillary column gas chromatography to pesticide residue analysis has been described by Ripley and Braun (1983). Two advantages of this technique are the high resolution achieved by the capillary column, which allows separation of many components in a complex mixture, often precluding the need for cleanup of sample extracts, and the reproducibility of retention time which gives a high degree of certainty during qualitative analysis. Concomitantly, the sharp, symmetrical peak shape and clearer retention time windows allow quantitation often a decade or more lower than that achieved with packed column gas chromatography.

All the examined parent compounds, metabolites, and derivatives chromatographed with a capillary column system (Ripley and Braun, 1983) producing unique re-

**Table IV. Gas Chromatographic Retention Time of Parent Acylalanine Fungicides and Some Metabolites and Derivatives on a SE-30 Capillary Column (Ripley and Braun, 1983)**

| compound | RRT[a] | compound | RRT[a] |
|---|---|---|---|
| metalaxyl | 0.89 | 2,6-dimethylaniline | 0.22 |
| CGA-29212 | 0.96 | metalaxyl acid[b] | 1.04 |
| chlorpyrifos | 1.00 | metalaxyl acid (OEt) | 0.98 |
| furalaxyl | 1.14 | 94689A (benzyl OH)[c] | 1.17, 1.25 |
| RE-26745 | 1.38 | 94689B (benzyl OH)[c] | 1.17, 1.28 |
| cyprofuram | 1.38 | 100255 (3-OH)[d] | 1.36 |
| oxadixyl | 1.39 | 100255 (3-OMe) | 1.23 |
| ofurace | 1.45 | 100255 (3-OEt) | 1.31 |
| benalaxyl | 1.51 | 108905 (benzoic acid)[be] | 1.20 |
| RE-26940 | 1.60 | 108905 ($COOCH_3$) | 1.20 |
| | | 108905 ($COOCH_2CH_3$) | 1.28 |
| | | ofurace alcohol | 1.41 |

[a] Relative retention time to chlorpyrifos (1.00 = 10.16 min). [b] Did not chromatograph well, low sensitivity. [c] Benzyl alcohol metabolites of metalaxyl (atropisomers). X,Y = rearrangement lactone, parent alcohol. [d] 3-Ring hydroxy metabolite of metalaxyl. [e] Benzoic acid metabolite of metalaxyl.

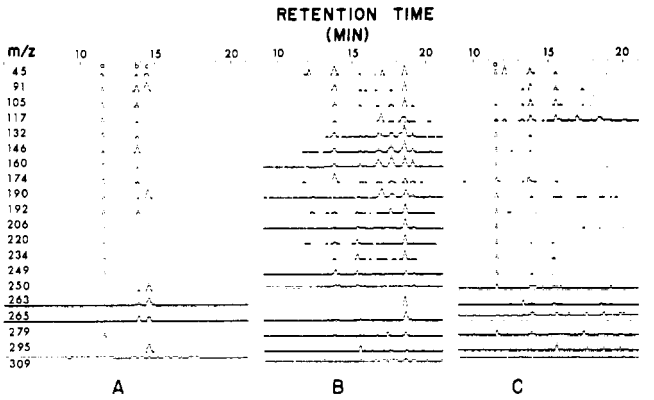


**Figure 3.** Multiple-ion monitoring chromatogram on SE-54 capillary column of (A) metalaxyl (a), benzyl alcohol (b), and ring 3-OH (c) metabolites, (B) check potato tuber extract, and (C) a field-treated potato tuber extract.

tention times (Table IV). On the SE-30 column, mixtures of cyprofuram and oxadixyl were only partially resolved. The acidic compounds (metalaxyl acid and benzyl acid metabolites) showed a low response and some peak tailing whereas after methylation, the expected response and symmetry were obtained. Depending on the injector temperature and the cleanliness of the capillary inlet system, metalaxyl benzyl alcohol may elute as the rearrangement lactone or as two peaks indicating some thermal decomposition, and ofurace often has a propensity to dechlorinate and elute as ofurace alcohol.

A nitrogen–phosphorus detector can be used to determine these compounds with good sensitivity and specificity to most crop extracts, even without cleanup. The mass selective detector in the multiple-ion monitoring mode coupled with the separation power of the capillary column adds a high degree of specificity to the determination. The common ions associated with the acylalanines and their metabolites allow simultaneous determination of these compounds in an extract (Figure 3). Cooke et al. (1982) used packed column GC and multiple-ion monitoring to confirm the presence of ofurace in potato foliage after soil treatment. Incorporation of partitioning or fractionation steps in the analytical methodology will also add specificity and confirmation to the analysis.

**Registry No.** CGA-48988, 57837-19-1; CGA-38140, 57646-30-7; SAN 371, 77732-09-3; RE-20615, 58810-48-3; RE-26745, 67932-71-2; RE-26940, 70622-00-3; CGA-29212, 52888-51-4; CGA-100255, 96258-85-4; CGA-100255 methyl ether, 96258-86-5; CGA-100255 ethyl ether, 96258-87-6; CGA-94689, 85933-49-9; CGA-94689 rearrangement lactone product, 96258-88-7; CGA-94689 methyl ether, 96258-89-8; CGA-94689 ethyl ether, 96258-90-1; CGA-108905, 96258-91-2; CGA-108905 methyl ester, 96258-92-3; CGA-108905 ethyl ester, 96258-93-4; benalaxyl, 71626-11-4; cyprofuram, 69581-33-5; metalaxyl acid, 87764-37-2; metalaxyl acid ethyl ester, 57837-86-2; ofurace alcohol, 66637-59-0.

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# Preparation and Use of Mixed Fumigant Standards for Multiresidue Level Determination by Gas Chromatography

James L. Daft

Two multicomponent stock concentrations of the following standard-grade fumigants are made in purified 2,2,4-trimethylpentane: methyl bromide, dichloromethane, carbon disulfide, chloroform, 1,2-dichloroethane, carbon tetrachloride, trichloroethylene, chloropicrin, 1,2-dibromoethane, and tetrachloroethylene. One concentration is used with electron-capture detection, the other with Hall detection. Analyst exposure to these toxic fumigant substances is minimized by fortifying samples and making working concentrations through single-step dilutions. Recovery data are accurate and complete. Single injections of the working concentrations permit rapid ppb level screening determination of residual fumigants in grain and grain-based products.

## INTRODUCTION

Most of the following fumigant methods were developed to determine 1–4 specific residues at levels above 1 ppm: leaching (Heuser and Scudamore, 1969; Berck, 1974; Fairall and Scudamore, 1980; Clower 1980), extraction and partition (Newsome and Panopio, 1982; Daft, 1983a), sweep and codistillation (Malone, 1969; Rains and Holder, 1981; Hughes et al., 1983; Iwata et al., 1983), headspace (Entz and Hollingfield, 1982; Page and Charbonneau, 1984; Bowers, 1984), and purge-closed loop (Wang and Lenahan, 1984). Recently, however, because of the attention given to the 1984 ban of the fumigant 1,2-dibromomethane (EDB) and because several residues from among about 15 commonly used fumigants can be detected in one sample

U.S. Department of Health and Human Services, Food and Drug Administration, Kansas City, Missouri 64106.