

GC/MS/MS Analysis For Pesticide Residues In Agricultural Products

GC/MS

Varian Application Note

Number 40b

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Introduction

The analysis of agricultural products for pesticide residues is of importance worldwide. Almost every country either imports or exports food. Most countries do both. The allowable residue requirements for an exporting country are often not the same as the importing country. There is an obvious need for test procedures that provide unambiguous results in the low ppb range for a wide variety of agricultural product matrices. The selectivity advantage of GC/MS/MS allows an analyst to quantitate and identify ultra trace level components in the most difficult matrices.

Experimental

GC/MS/MS provides extreme selectivity against matrix interference through three separation mechanisms: (1) chromatographic separation on the GC column with the accompanying knowledge of the retention time for target analytes, (2) isolation of a characteristic pesticide/fungicide characteristic ion, and (3) dissociation of the isolated ion to a unique set of product ions which unambiguously identifies the presence or absence of the targets. (For more information refer to the References.) The optimum Collision Induced Dissociation (CID) voltage must be determined for each parent ion of the target pesticides. This is accomplished conveniently through the use of the Toolkit software which allows the CID voltage to be incremented on a scan by scan basis. In Figure 1 we see the results of this injection. Notice that the degree of dissociation of the parent ion is changing as the CID voltage is increased from one scan to the next scan.

This allows the analyst the luxury of quickly determining the optimal conditions for a target analyte. This method optimization feature is time programmable throughout the chromatogram so that a whole series of compounds can be optimized in a single injection.

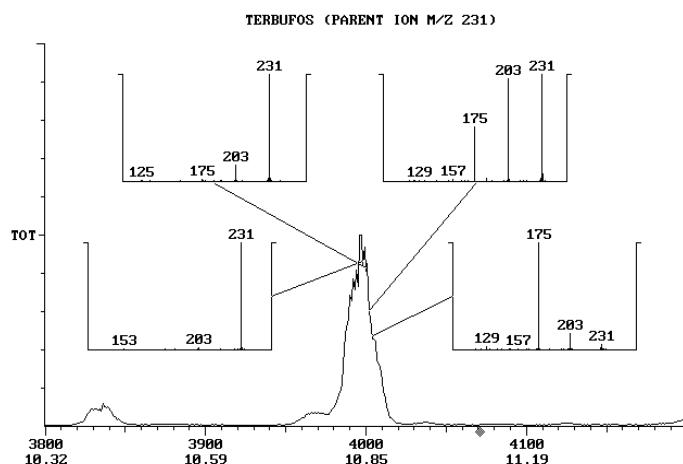


Figure 1: Automatic method optimization allows the CID voltage to be incremented on a scan by scan basis.

Twenty-one pesticides and five agricultural products were studied to determine accuracy, reproducibility and typical method detection limits in an attempt to correlate the performance of benchtop GC/MS/MS to pesticide residue analysis. The samples were prepared by first homogenizing the individual products followed by a methylene chloride extraction of the residual pesticides. The extracts were filtered and concentrated to a known volume. A portion of the extracts was spiked with the equivalent of 20 ppb of each pesticide. A 20 ppb spike under the conditions used for this analysis gives 100 pg on column for each analyte as well as the soluble portion of 5 mg of the agricultural product. The spiked and unspiked samples were analyzed by GC/MS/MS.

Discussion

Virtually every pesticide has a coeluting background component associated with it. In the case of the orange extract, a target analyte (Chlorneb) has a coeluting compound with a major ion at the same mass as the parent ion for Chlorneb. This ion (m/z 191) if chosen for quantitation by EI GC/MS in either the full scan or SIM mode of operation would give a large positive interference. Figure 2 shows the MS/MS chromatogram and Spectrum of the interfering compound. In Figure 3, we see the MS/MS spectrum of Chlorneb using m/z 191 as the parent ion.

The product ion for Chlorneb of m/z 163 is not found in the MS/MS spectrum of the coeluting compound, and as such, this ion can be used to successfully quantitate Chlorneb in the extract. Table 1 shows the quantitative recovery of a 20 ppb spike into the 5 matrices tested.

Eight replicate injections were made for each sample to determine the accuracy and standard deviation. Method detection limits were calculated by multiplying the standard deviation by the Student's t value (3.0) for 8 replicates at the 99% confidence level. Where there is no data point in the table, an interference was observed indicating that additional method optimization is needed for some compounds in some matrices.

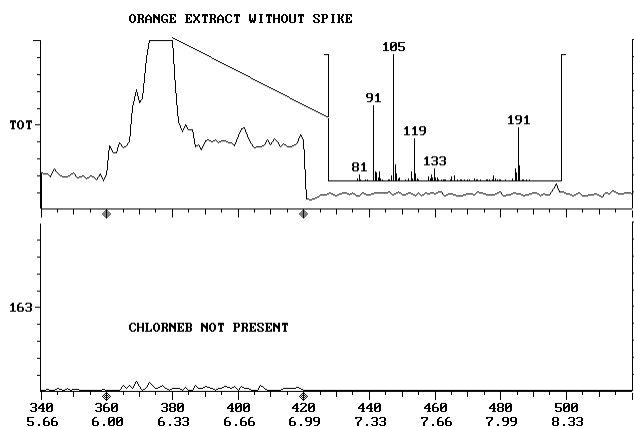


Figure 2: Orange extract with large interference that coelutes with Chlorneb.

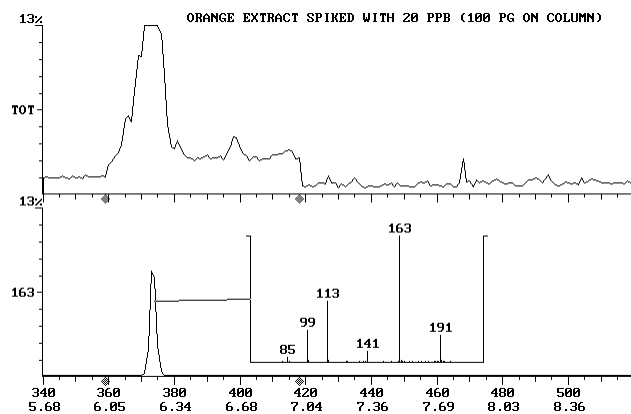


Figure 3: Orange extract with 20 ppb Chlorneb spiked into the sample.

- | | |
|---------------------------|-------------------------|
| 1. METHYLNAPHTHALENE | 12. MALATHION |
| 2. DICHLOBENIL | 13. DURSBN |
| 3. ETRIDIAZOLE | 14. DIPHENAMID |
| 4. CHLORNEB | 15. α -CHLORDANE |
| 5. TRIFURALIN | 16. γ -CHLORDANE |
| 6. BHC | 17. OXADIAZON |
| 7. CLOMAZONE | 18. CHLOROPROPYLATE |
| 8. TERBUFOS | 19. ETHION |
| 9. PHENANTHRENE D-10 (IS) | 20. FAMPHUR |
| 10. CHLOROTHALONIL | 21. DDT |
| 11. DICHLOFENTHION | 22. METHOXYCHLOR |

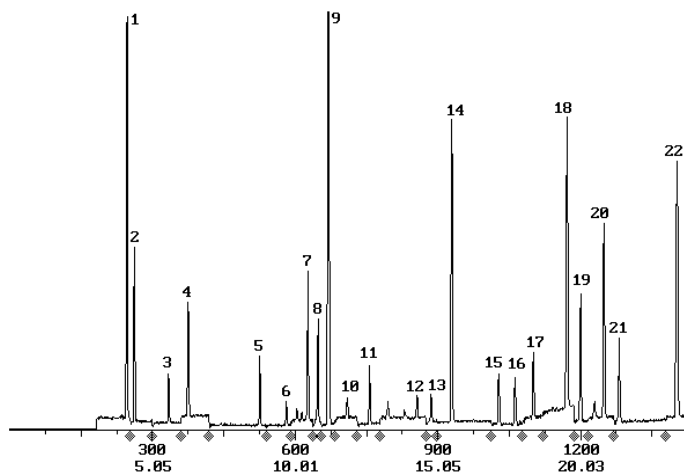


Figure 4: GC/MS/MS chromatogram of pesticide standard mix (100 pg on column). Diamonds on the X-axis indicate time-programmed changes in MS/MS conditions.

Table 1: Recovery of 20 ppb Spiked Extracts (N=8)

Compound	Standard	Orange	Strawberry	Tomato	Onion	Broccoli
Methyl Naphthalene	19	25	20	18	22	20
Dichlobenil	19	24	18	17	11	19
Etridiazole	20	22	21	22	16	12
Chlorneb	20	26	22	18	19	20
Trifuralin	20	27	19	16	18	22
BHC	20	24	22	17	15	18
Clomazone	19	21	23	15	15	18
Terbufos	20	22	15	15	13	16
Chlorothalonil	22	24	25	15	6	21
Dichlofenthion	20	23	22	16	16	21
Malathion	19	23	21	15	15	14
Dursban	20	22	25	16	19	22
Diphenamid	20	28	29	17	22	26
Alpha Chlordane	19	25	23	16	20	18
Gamma Chlordane	20	26	23	16	20	19
Oxadiazon	20	25	23	18	23	22
Chlorpropylate	20	25	25	20	28	27
Ethion	19	30	24	20	27	25
Famphur	20	27	21	20	26	25
DDT	20	21	22	19	21	-
Methoxychlor	20	25	20	20	19	-

Table 2: Method Detection Limits in ppb (N=8)

Compound	Standard	Orange	Strawberry	Tomato	Onion	Broccoli
Methyl Naphthalene	1	4	3	2	3	2
Dichlobenil	1	6	2	2	2	1
Etridiazole	2	6	2	5	3	12
Chlorneb	1	3	2	2	2	2
Trifuralin	6	4	3	2	2	4
BHC	2	3	1	3	1	6
Clomazone	2	5	1	2	1	6
Terbufos	2	4	2	3	2	2
Chlorothalonil	8	10	5	8	7	6
Dichlofenthion	2	5	2	1	1	1
Malathion	3	3	3	1	2	8
Dursban	2	7	2	2	2	2
Diphenamid	2	8	2	2	2	6
Alpha Chlordane	3	4	2	3	2	9
Gamma Chlordane	2	5	2	2	2	10
Oxadiazon	2	2	2	2	2	8
Chlorpropylate	2	3	2	2	2	9
Ethion	1	5	2	2	2	8
Famphur	1	5	2	3	2	16
DDT	2	11	6	13	11	-
Methoxychlor	2	9	5	16	11	-

Table 3: MS/MS Conditions

Compound	Parent Ion	Amplitude	Excitation Storage
Methyl Naphthalene	141	86	75
Dichlobenil	171	65	60
Etridiazole	211	57	75
Chlorneb	191	55	65
Triburalin	306	45	75
BHC	219	45	65
Clomazone	204	54	65
Terbufos	231	54	75
Phenanthrene d-10 (IS)	188	90	75
Chlorothalonil	266	71	75
Dichlofenthion	279	54	75
Malathion	173	37	60
Dursban	314	42	75
Diphenamid	167	61	60
Alpha Chlordane	373	61	100
Gamma Chlordane	373	61	100
Oxadiazon	258	42	75
Chloropropylate	251	57	75
Ethion	231	51	75
Famphur	218	57	75
DDT	235	63	75
Methoxychlor	227	75	80

Instrument Conditions

Gas Chromatograph

Column: Amine deactivated 5% phenyl/95% methyl PDMS, Varian equivalent: CP-Sil 8 CB for amines, # CP7595 30 m x 0.25 mm, df = 0.5 µm

Flow rate: 1 mL/min

Oven program: 150°C with no hold, 5°/min to 290°C, hold for 10 min

Injection temp: 280°C

Transfer line: 280°C

Injection mode: split

Split Ratio: 20/1

Injection Volume: 2 µL

Mass Spectrometer

Mass range: 70-400

Scans/sec: 1

Mult. delay: 3 min

RF level: 48u

Filament: 90

Threshold: 0

Ion trap: 220°C

References

- Application Note 27: GC/MS/MS with a Benchtop Mass Spectrometer
- Advantage Note 3: GC/MS/MS Analysis for Target Analytes in a Complex Matrix
- Advantage Note 5: GC/MS/MS as a Separations Technique

Conclusion

The Saturn 3 equipped with the MS/MS option can analyse for pesticide residues in agricultural products at low ppb levels. The results are accurate and reproducible in very complex matrices.

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*These data represent typical results.
For further information, contact your local Varian Sales Office.*