

# JMS Letters

Dear Sir,

## Rapid and Sensitive Determination of Pesticides in Environmental Samples by Accelerated Solvent Extraction and Tandem Mass Spectrometry

Two recent commercial innovations have made it possible to analyze soil samples rapidly for pesticides in the low-ppb range. Gas chromatography/ion trap tandem mass spectrometry (GC/MS/MS) coupled with accelerated solvent extraction (ASE) has increased the sensitivity and speed, respectively, of environmental analysis. ASE can quantitatively remove organic compounds from soil samples in  $\sim 15$  min,<sup>1</sup> while the GC/MS/MS can detect compounds at the low-ppb level in complex matrices.<sup>2</sup> ASE pumps a solvent at elevated temperature and pressure into a cell containing the sample and, after a specified time period, the solvent is transferred to a collection vial. Unlike the labor- and time-intensive sonication or Soxhlet extraction procedures,<sup>3</sup> the ASE apparatus is automated.

The solvent containing the extracted organic compounds may need an additional clean-up owing to the exhaustive extraction that results in removal of non-volatile/non-target components (as well as the target analytes) from the soil. GC/MS/MS is ideal for analyzing low-level samples with high non-volatile/background content. GC/MS/MS accomplishes a 'clean-up' step by trapping the precursor ion and removing the unwanted co-eluting background ions before subsequent collision to produce a unique fragment ion. This step is performed in the trap manifold, after GC separation, and enhances sensitivity by eliminating background noise that normally would obscure the signal. Together these complementary techniques were used for a rapid low-level pesticide analysis on a standard reference material and an environmental sample.

All extractions were performed on a Dionex (Sunnyvale, CA, USA) ASE 200 accelerated solvent extractor. A 7 g amount of NIST SRM 1941 Marine Sediment or 10 g of a Superfund soil sample (sieved to 10 mesh) were placed in a 11 ml stainless-steel extraction cell. The extraction conditions were as follows: system pressure, 14 MPa (2000 psi); oven temperature, 100 °C; oven heat-up time, 5 min; static time, 5 min; solvent, hexane-acetone (1:1, v/v); flush volume, 6.6 ml; nitrogen purge, 1 MPa (150 psi) for 60 s; and final volume, 18 ml.

Although the warm recovered extracts were clear, solid matter would precipitate upon standing at room temperature. In such cases, the extract was centrifuged at low speed and the

supernatant decanted. An aliquot of each extract was concentrated by a factor of 5 under a gentle nitrogen stream at 50 °C.

A 0.5 ml portion of the concentrate was transferred to an autosampler vial and internal standard stock solution added to give a final concentration of 5.0 ng  $\mu\text{l}^{-1}$ . The internal standard was *p*-terphenyl-*d*<sub>14</sub> for the chlordane components and 2,2',3,4,4',5,6,6'-octachlorobiphenyl (OCBP) for the remaining pesticides.

Calibration standards at concentrations of 10, 20, 50 and 100 pg  $\mu\text{l}^{-1}$  with 5 ng  $\mu\text{l}^{-1}$  of the appropriate internal standard were prepared in hexane and 0.5  $\mu\text{l}$  was injected. The average response factor for each analyte (over the entire concentration range and normalized to the internal standard) was calculated and used for quantitation.

A Varian (Walnut Creek, CA, USA) Saturn 3 gas chromatograph and ion trap with MS/MS capability with a septum programmable injector (SPI) was used to analyze the soil extracts. The temperature program consisted of an initial 2 min hold at 60 °C followed by a temperature ramp at 10 °C  $\text{min}^{-1}$  to 180 °C, then at 6 °C  $\text{min}^{-1}$  to 264 °C followed by 10 °C  $\text{min}^{-1}$  to a final temperature of 304 °C. The transfer line was held at 300 °C and the manifold at 260 °C. All injections were 0.5  $\mu\text{l}$ . The column was a J&W (Folsom, CA, USA) 30 m  $\times$  0.25 mm i.d. DB-5 (methylpolysiloxane containing 5% phenyl groups), 0.25  $\mu\text{m}$  film thickness. The SPI injector contained a Restek (Bellefonte, PA, USA) inlet sleeve with buffer (catalog No. 20850) packed with 1 cm of deactivated glass-wool. A 1 m  $\times$  0.53 mm i.d. retention gap was installed to improve the peak shape and protect the analytical column. The SPI injector was held at 60 °C for 0.5 min, then heated to 300 °C in 1 min and held for 5 min.

The GC/MS/MS system was scanned from either 150 u (for the chlordane components) or 100 u (for the remaining pesticides) to the molecular ion cluster at 0.6 s per scan. This ensured that three microscans were performed every 0.6 s (and the average recorded as one scan). The Saturn 3 software was version 5.2. The MS/MS parameters are shown in Table 1. The significance of the parameters is described in Ref. 2.

The reported non-certified concentrations of chlorinated pesticides in NIST SRM 1941, Organics in Marine Sediment, were obtained by GC with electron-capture (ECD).<sup>4</sup> Comparison with our MS/MS results (see Table 2) shows good agreement down to the method detection limit (the low-ppb range) depending on the analyte. Some of the pesticides were determined in duplicate, including recalibration.

Pesticide spectra obtained by ion trap MS/MS contained the same *m/z* ions as the ion trap electron impact (EI) spectra, but the abundances were shifted to lower *m/z*. The reason for

Table 1. MS/MS parameters

Compound	Parent ion ( <i>m/z</i> )	Window ( <i>m/z</i> )	Excitation time (ms)	Excitation amplitude (V)	R.f. storage ( <i>m/z</i> )	Quantitation/product ion ( <i>m/z</i> )
$\gamma$ -Chlordane	373.8	4	30	41.75	71.7	266
$\alpha$ -Chlordane	373.8	4	30	41.75	71.7	266
<i>trans</i> -Nonachlor	407.8	4	30	38.25	71.7	300
<i>p</i> -Terphenyl- <i>d</i> <sub>14</sub>	244.2	1	50	64	71.7	236
Dieldrin	262.85	6	30	73	79.6	191 + 193
4,4'-DDE	246.9	4	30	64	71.7	176
4,4'-DDD	235.9	4	40	61.5	71.7	165
4,4'-DDT	235.9	4	40	60.5	71.7	199
OCBP	429.8	6	30	88.5	111.5	358 + 360

**Table 2. Soil extraction results (concentrations in ppb)**

Compound	SRM 1941		Superfund soil	
	GC/ECD	GC/MS/MS	GC/ECD	GC/MS/MS
$\alpha$ -Chlordane	2.06	2.2	44	1.8
$\gamma$ -Chlordane	—	2.2	31	1.4
<i>trans</i> -Nonachlor	0.97	0.9	—	0.5
Dieldrin	0.63	ND <sup>a</sup>	220	ND
		ND		ND
4,4'-DDE	9.71	8.6	1500	1380
		9.9		1420
4,4'-DDD	10.3	10.4	630	47
		9.6		47
4,4'-DDT	1.11	2.2	1100	1310
		2.2		1320

<sup>a</sup> ND = not detected.

using MS/MS instead of EI analysis is that, unlike ion trap EI, MS/MS is not affected by the background signal or co-eluting peaks.

Analysis of the EPA Superfund soil by sonication/Soxhlet and GC/ECD is complicated by a high concentration of toxaphene (6100 ppb reported). This chromatogram displays an almost continuous distribution of peaks, co-eluting with all of the other analytes. Positive interferences in ECD probably explain the generally lower concentrations obtained by MS/MS. GC/ECD has a lower method detection limit than GC/MS/MS. However, this may not be realized when interferences are present. Figure 1 shows a 50 pg  $\alpha$ -chlordane standard tandem mass spectrum (bottom) and the  $\alpha$ -chlordane tandem mass spectrum (top) found in SRM 1941. At the 2.2 ppb level (see Table 2), the soil extract still contains the  $m/z$  264, 266, 301 and 303 ions of the 50 pg standard.

In our hands, quantitative extraction of SRM 1941 took 10 min whereas Soxhlet can take as long as 8–24 h,<sup>3</sup> a significant improvement. Also demonstrated was GC/MS/MS sensitivity, adequate for the detection of low-picogram levels (i.e. ECD

levels) of pesticides. The combination of ASE and GC/MS/MS was shown to represent complementary techniques for the determination of pesticides in soil and were either comparable to or better than existing technologies in terms of speed, sensitivity and reliability.

### Acknowledgements

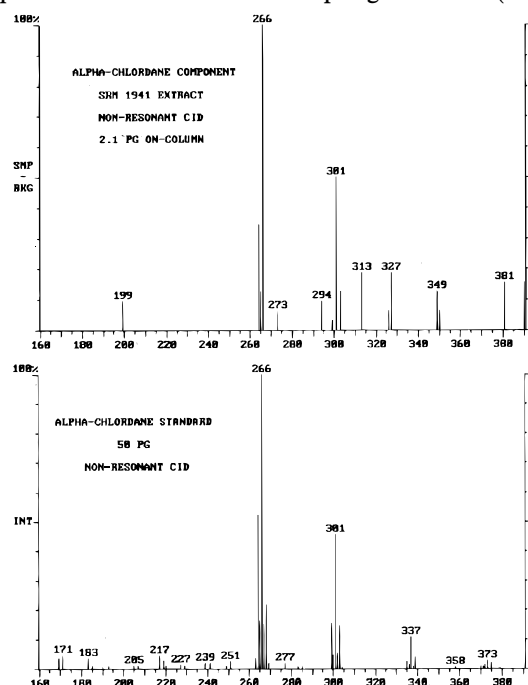
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Yours,

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**Figure 1.** Non-resonant collision-induced dissociation of  $\alpha$ -chlordane in sample and standard.

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