Analyzing Phenyl Ureas and Carbamate Pesticides Using ESI-, APPI-, and APCI-LC/MSD

Application

Environmental and Food

Author

Chin-Kai Meng
Agilent Technologies, Inc.
2850 Centerville Road
Wilmington, DE 19808-1610
USA

Abstract

Carbamates (a class of highly effective insecticides) and phenyl ureas (a class of herbicides) were successfully analyzed by liquid chromatography/mass spectrometry using electrospray ionization (ESI), atmospheric pressure chemical ionization (APCI), and atmospheric pressure photo ionization (APPI) sources. APPI and APCI exhibited lower background signals and fewer background peaks than ESI. Phenyl ureas, in general, exhibited better signal-to-noise ratios (S/N) from APCI or APPI than from ESI. However, it was just the opposite for carbamates. The S/N was better from ESI than from APCI or APPI. A small amount of post-column acetone was needed in the APPI source as a photoionizable dopant for charge transfer to the analyte.

Introduction

Carbamates, a class of highly effective insecticides, are widely used worldwide to protect crops from pests. Phenyl ureas, a class of herbicides, are highly potent chemicals for agricultural weed control. All are potential endocrine disrupters found in ground- and surface-water samples.

Gas chromatography/mass spectrometry (GC/MS) systems have traditionally been used for analyzing pesticides in environmental samples. Due to the thermally labile nature of these compounds, liquid chromatography has been the method of choice for the separation of these pesticides. Many of the pesticides within the same class exhibit similar ultraviolet (UV) spectra. With the development of atmospheric pressure ionization (API) techniques, liquid chromatography/mass spectrometry (LC/MS) systems have become the preferred method for the analysis of ground- and surface-water contaminants. The LC/MS provides better sensitivity and specificity than typical diode array detectors (DAD), even if the analytes are not fully resolved from neighboring eluants.

Three different API sources were used in this study for comparison: electrospray ionization (ESI), chemical ionization (APCI) [1], and photo ionization (APPI) [2]. In ESI, the ionization process happens before the solvent evaporation process. It is, therefore, a more universal ionization for polar compounds. In APCI and APPI, the analyte is not ionized until after solvent evaporation. APCI involves a charge transfer (proton or electron) between ionized reagent gas and the analyte. APPI requires that the analytes and/or a dopant be photoionized by absorbing photons from the 10.6 eV krypton light. The dopant then transfers the charge to the analyte, which could be thought of as photon-induced chemical ionization.

Experimental

A mixture of carbamates and urea pesticides at 10 ppm (ng/µL) in acetonitrile was purchased from AccuStandard (New Haven, CT). A series of dilutions in acetonitrile were made for the linearity studies. The compounds and their structures are shown in Figures 1 and 2, respectively. All experiments were performed on two G1946D LC/MSD systems equipped with ESI on one and APCI/APPI on the other. The LC/MS conditions are listed in Table 1.

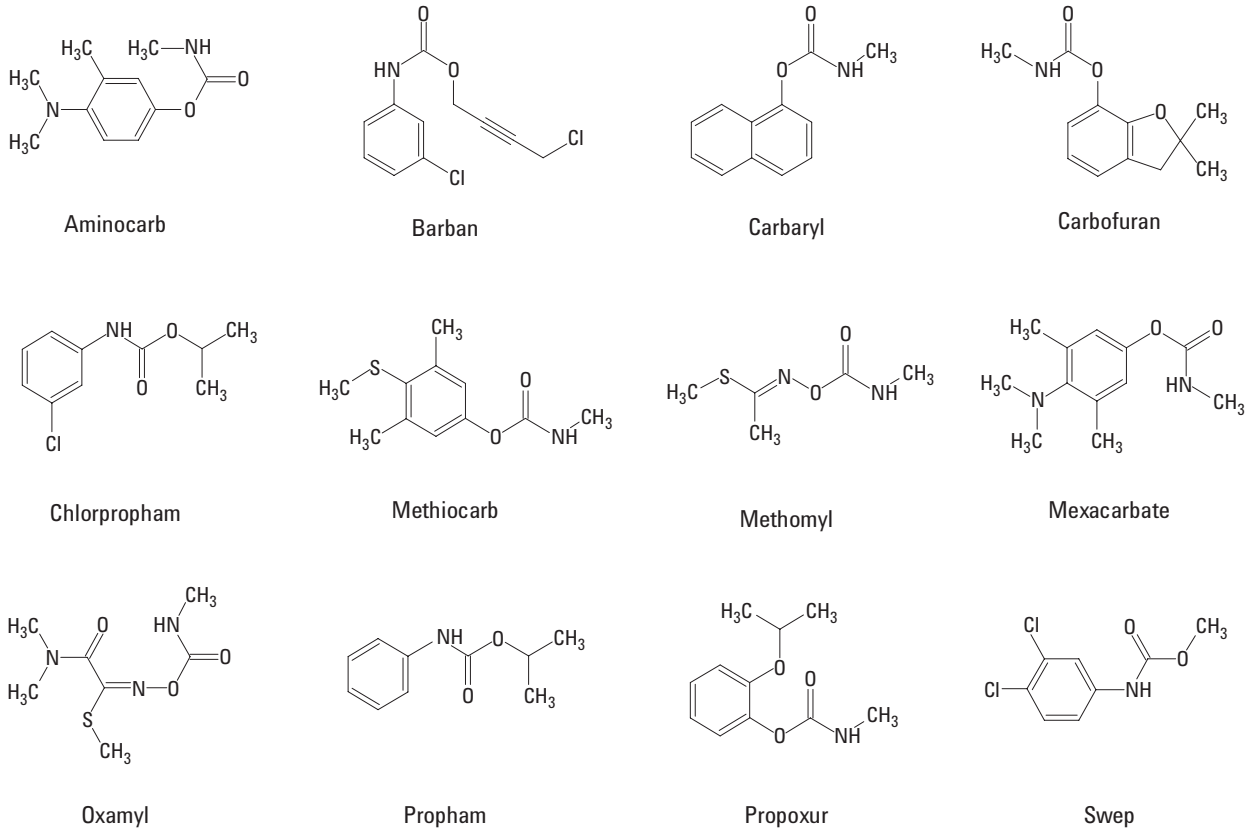


Figure 1. The 12 carbamates used in this study.

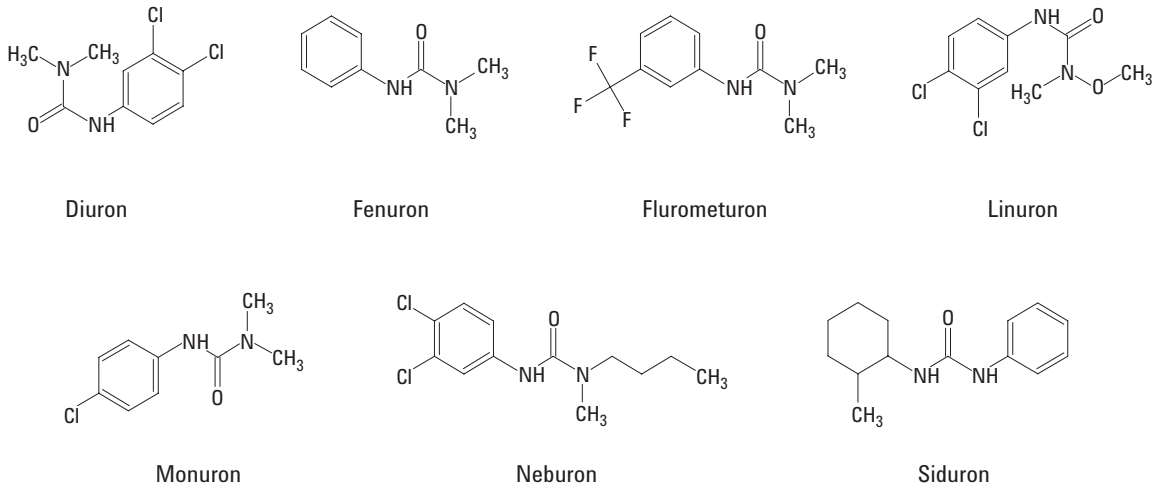


Figure 2. The seven phenyl ureas used in this study.

Table 1. LC/MS Conditions

	ESI	APCI	APPI
Column	Zorbax Eclipse XDB-C8, 4.6 x 50 mm, 3.5 µm (p/n 935967-906)		
Column temperature	30 °C	30 °C	30 °C
Column flow rate	1 mL/min	1 mL/min	1 mL/min
Solvent A	H_2O, 0.1% acetic acid or as specified	H_2O	H_2O
Solvent B	Acetonitrile, 0.1% acetic acid or as specified	Acetonitrile	Methanol
Post column	n/a	n/a	40 µL/min acetone added as dopant
Solvent gradient	B: 10% at 0 min, 30% at 4 min, 80% at 10 min, 80% at 16 min	B: 30% at 0 min, 40% at 4 min, 70% at 13 min, 80% at 16 min or as specified in the figure	
Injection volume	2 µL	2 µL	2 µL
Drying gas flow	12 L/min	11 L/min	11 L/min
Drying gas temperature	350 °C	275 °C	275 °C
Fragmentor voltage	60 V	110 V	110V
Vcap	3500 V	4500 V	4500V
Nebulizer pressure	60 psi	35 psi	35 psi
Vaporizer	n/a	225 °C	225 °C
Step size	0.1	0.1	0.1
Peak width (min)	0.15	0.15	0.15
Time filter	Off	Off	Off
Scan (*m/z*)	150–800	115–500	115–500
Polarity	Positive	Positive	Positive

Results and Discussion

Figure 3 shows the effect of adding a post-column dopant (acetone) in APPI to significantly improve the responses of the analytes. Acetone at a flow rate of 40 µL/min was introduced to the column effluent before entering the nebulizer. A gain of 1000× in peak height was seen for some of the analytes. The difference in peak-height gain among the analytes may be due to their structural difference and the charge transfer efficiency with the dopant.

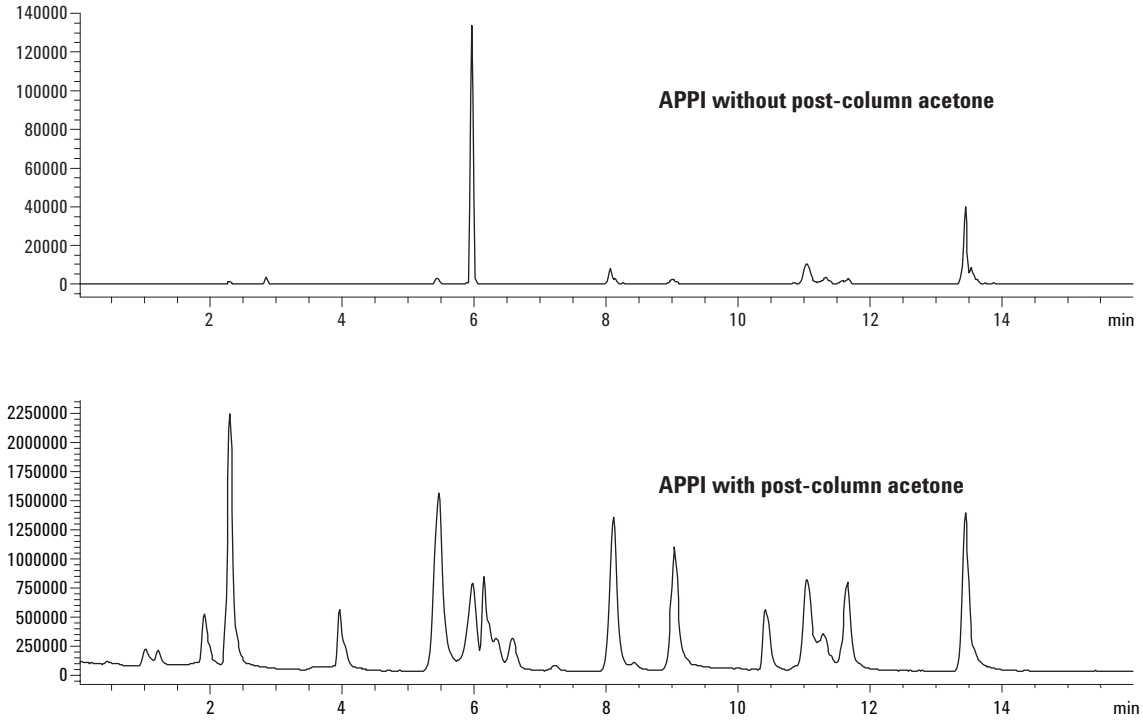


Figure 3. TICs show the effect of adding post-column acetone to enhance analyte signal in APPI. Methanol was used as solvent B for both TICs.

The LC mobile phase in APPI can interfere with ionization if the solvent has more affinity for the proton than the analyte. Figure 4 shows that acetonitrile can be a problem for baseline stability and it is always best to also try methanol in APPI.

Typical background spectra between 15 and 15.5 minutes from the three sources appear in Figure 5. Because ESI is a more universal ionization source for polar compounds and ionic modifiers are used in ESI, the baseline has a lot more peaks and the noise is usually 5 to 15 times higher than APCI and APPI.

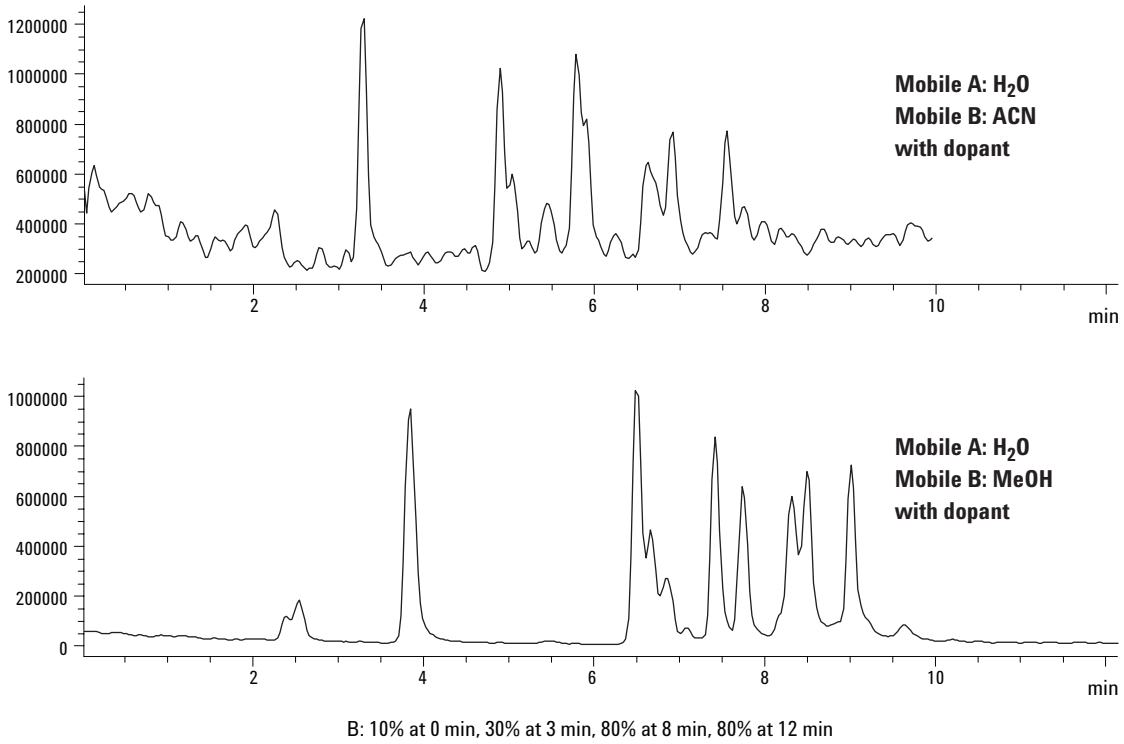


Figure 4. TICs show that methanol is a better mobile phase than acetonitrile in APPI. Acetone was used as dopant.

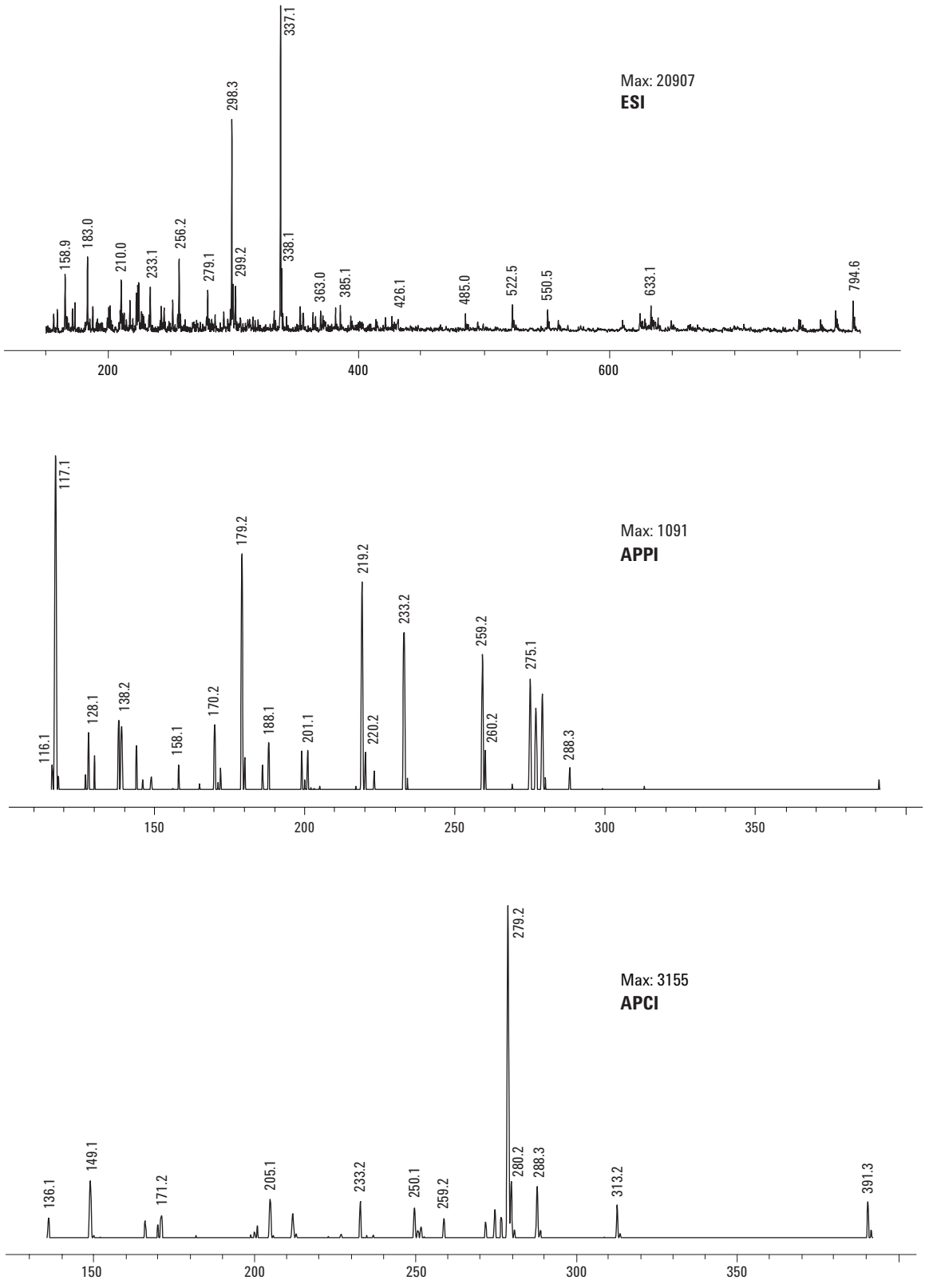
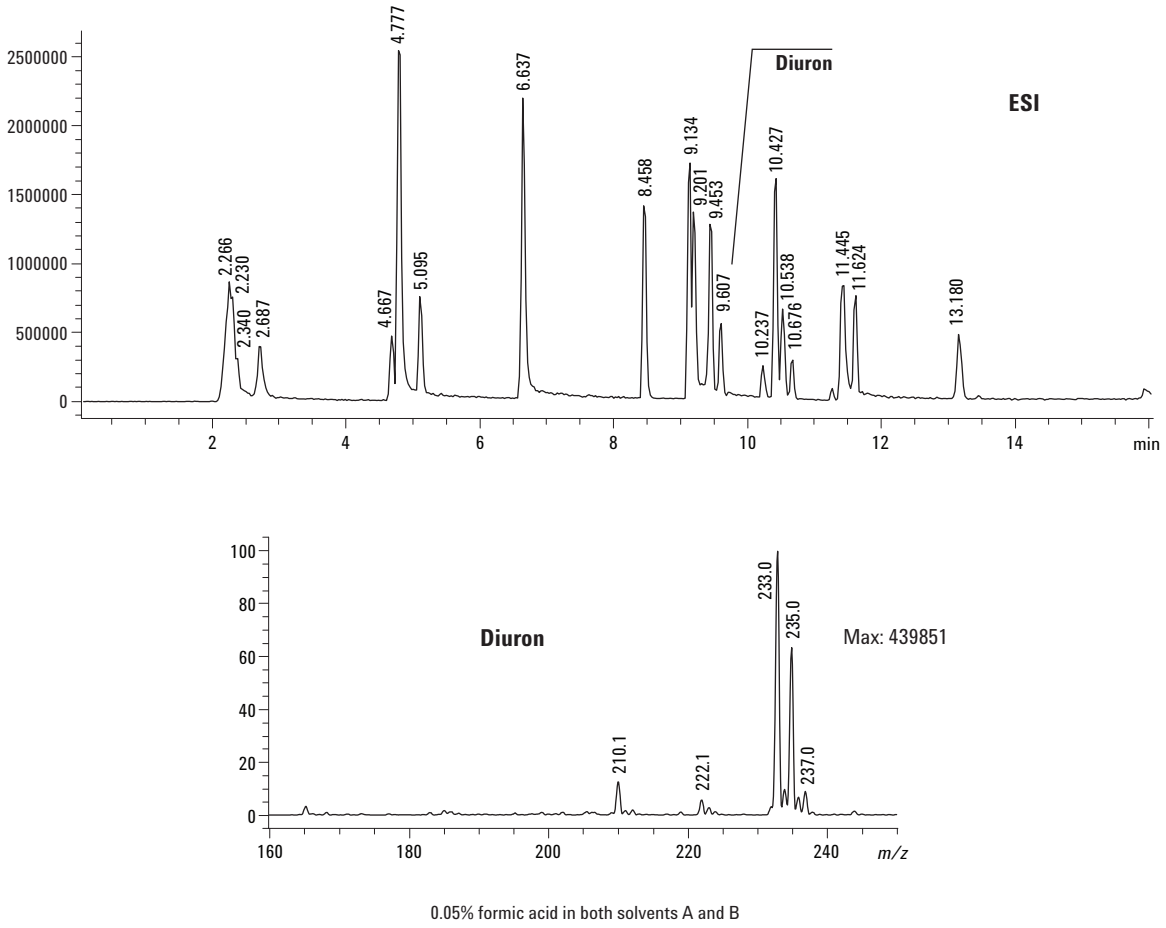


Figure 5. Baseline noise of the three sources are compared. ESI exhibits higher noise and more peaks in the baseline.

The spectra of 20 ng Diuron on column from the three sources (ESI, APCI, and APPI) appear in Figures 6, 7, and 8. The peak at mass 233 is the $[M+H]^+$ peak. Peaks at masses 233, 235, and 237 match the isotope peak-intensity pattern for two chlorine atoms, which is additional information for compound confirmation. Although ESI gives better response compared to the other two sources, it has lower signal-to-noise ratio (S/N).



0.05% formic acid in both solvents A and B

Figure 6. The TIC of all target compounds from ESI. The bottom half is the ESI spectrum of 20 ng Diuron on column.

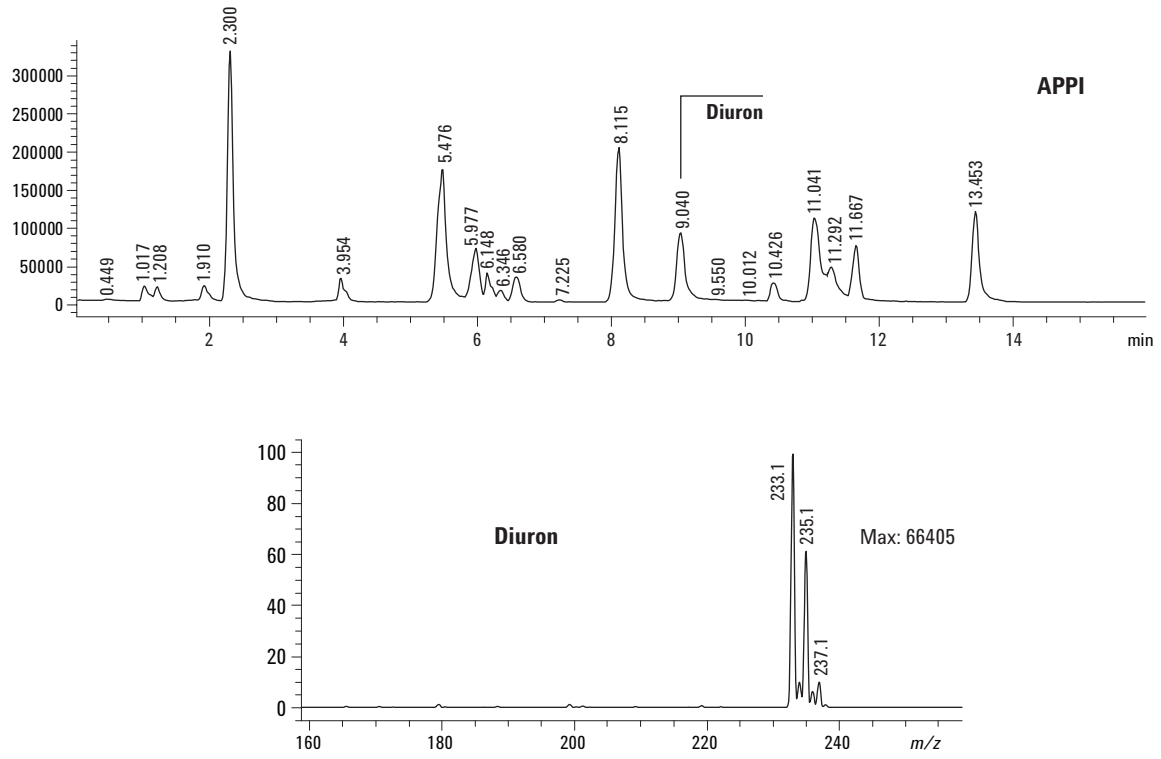


Figure 7. The TIC of all target compounds from APPI. The bottom half is the APPI spectrum of 20 ng Diuron on column.

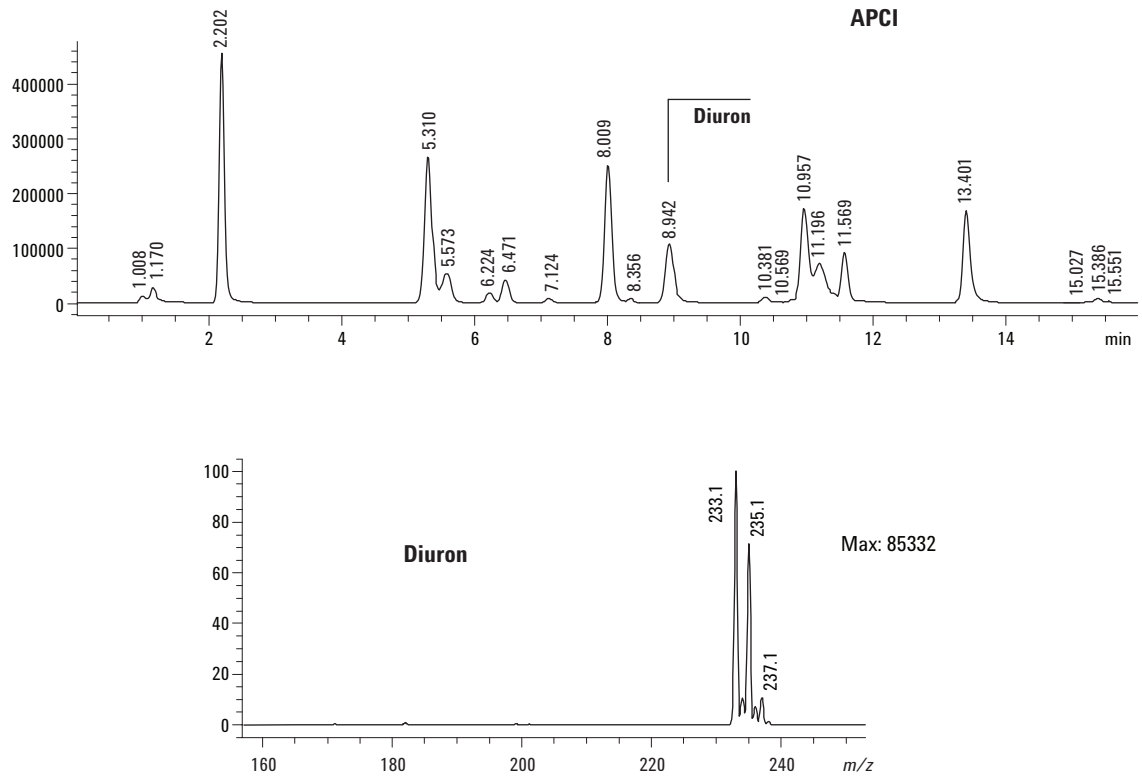


Figure 8. The TIC of all target compounds from APCI. The bottom half is the APCI spectrum of 20 ng Diuron on column.

Figure 9 shows the spectra of Siduron (protonated ion at *m/z* 233) from all three sources. Protonated dimer (*m/z* 465) and sodiated dimer (*m/z* 487) of Siduron are fairly significant peaks in the ESI spectrum. However, only negligible amounts of protonated dimers (no sodiated dimers) were observed in the APPI and APCI spectra. This is mainly due to the different sequence of desolvation and ionization steps. In ESI, ionization happens before desolvation. In APPI and APCI, ionization comes after desolvation.

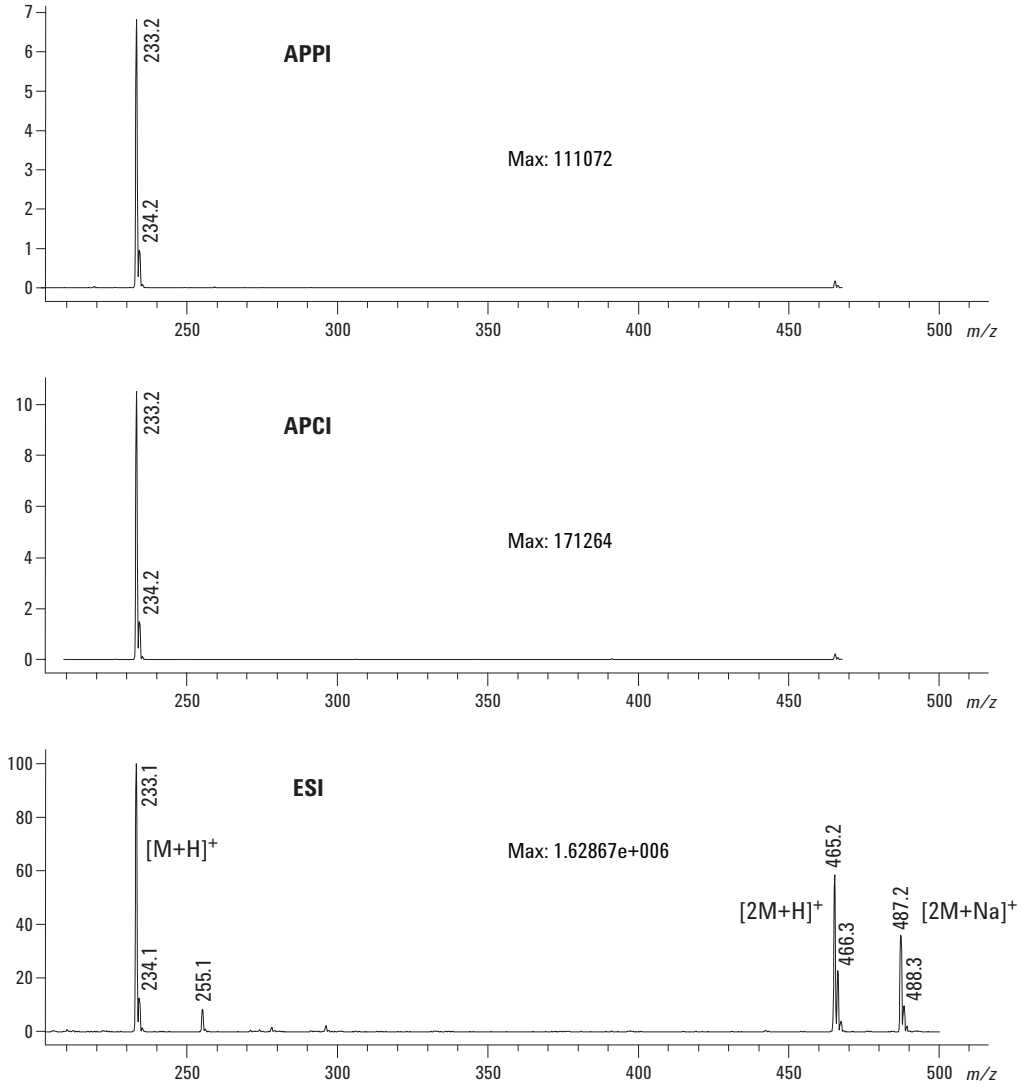


Figure 9. Spectra of Siduron from APPI, APCI, and ESI. Significant dimer peaks are observed in ESI.

Figure 10 compares the S/N of some of the target compounds analyzed by the three sources. The figure shows that carbamates, in general, give better S/N from ESI than from APCI or APPI. However, it is just the opposite for phenyl ureas, for example, the S/N is better from APCI or APPI than from ESI. It is also worth noting that APPI shows consistently higher S/N than APCI for this study.

A calibration based on the Methomyl $[M+H]^+$ (*m/z* 163) is linear over the concentration range of 20–2000 pg on column. Figure 11 shows the ESI calibration curve with the linear correlation coefficient of 0.9996. Four of the Methomyl peaks that were used for the linearity calibration appear in Figure 12.

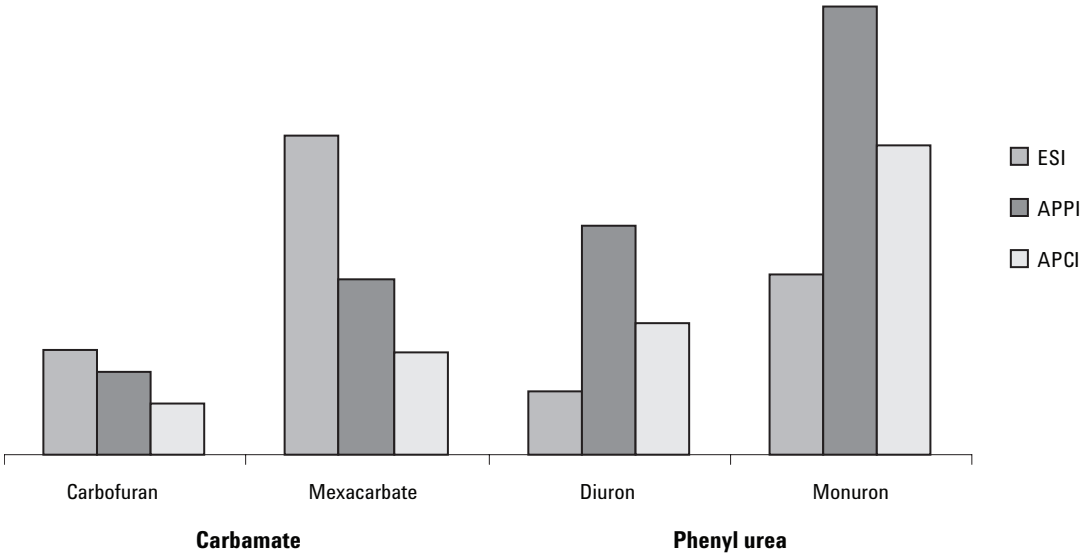


Figure 10. The S/N of four analytes from the three ionization modes.

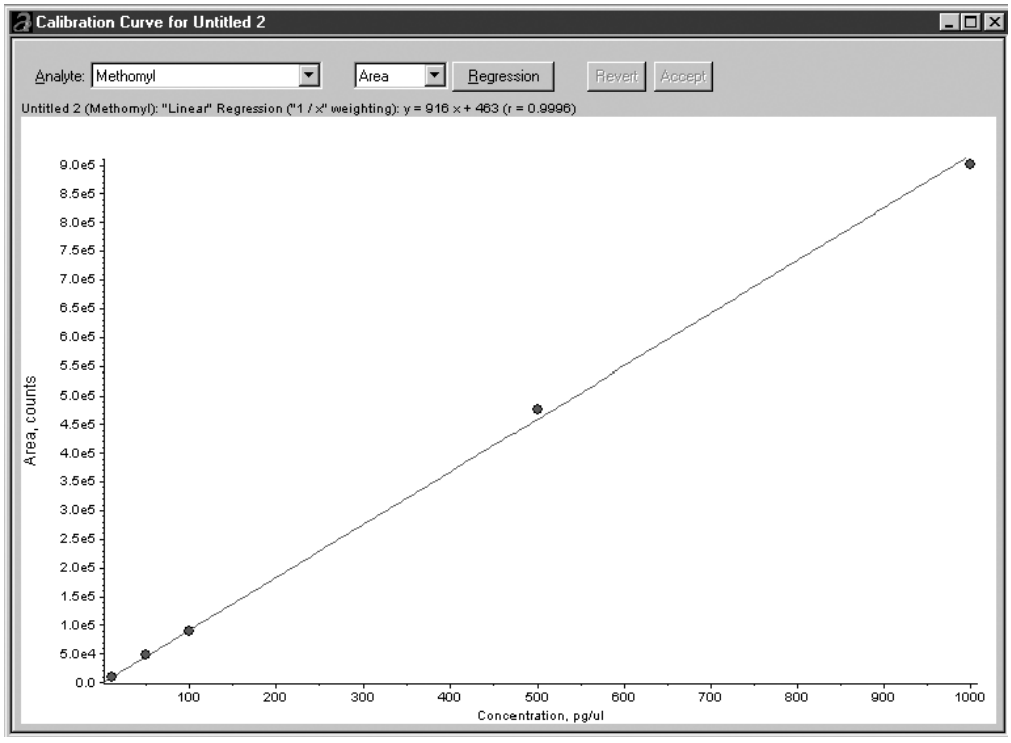


Figure 11. The calibration curve of Methomyl, by ESI in SIM mode (mass 163), shows good linearity over the concentration range of 20–2000 pg on column (2-µL injection).[1]

[1]The calibration curve was generated using the PE Sciex Analyst™ software.

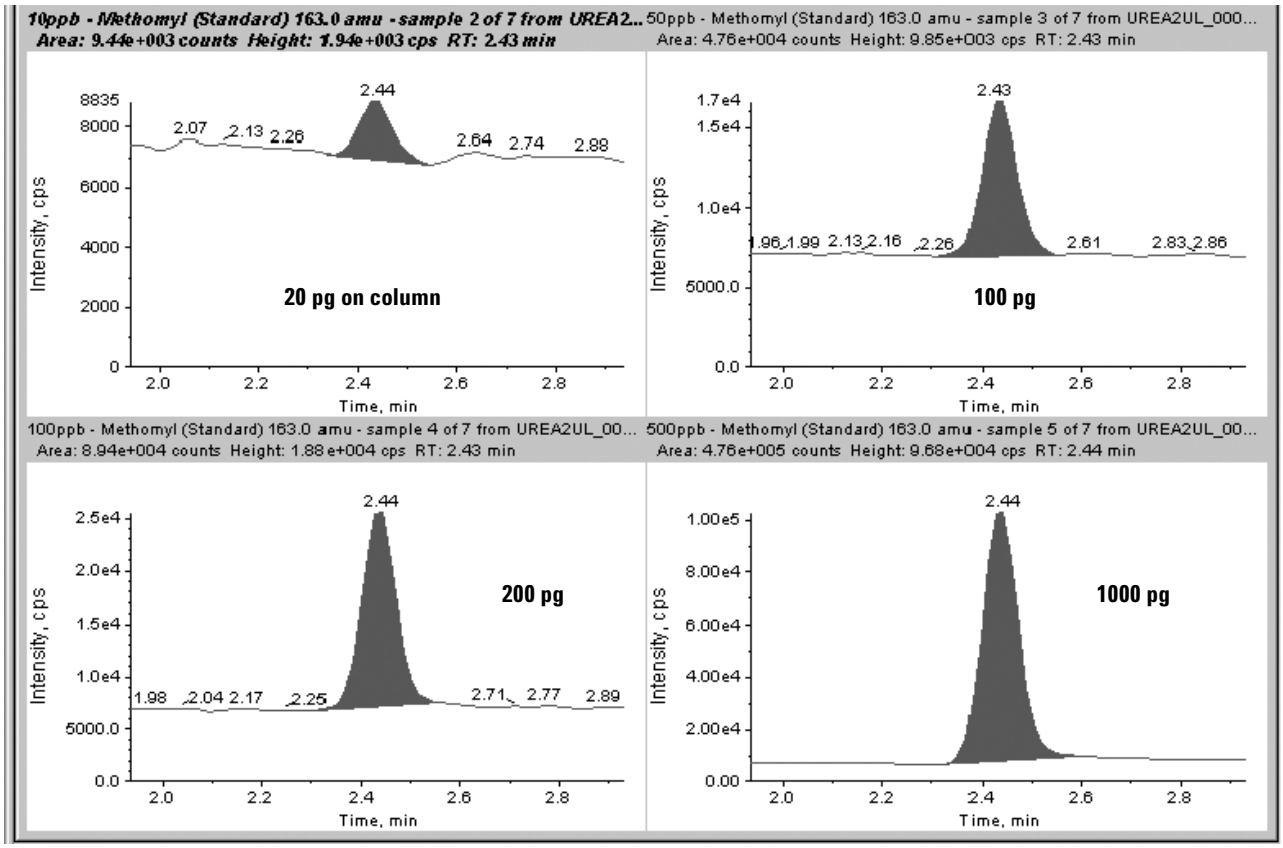


Figure 12. The Analyst™ software shows four of the Methomyl peaks (163 amu) that were used for generating the calibration curve in Figure 11.

Three different modifiers (formic acid, ammonium acetate, and acetic acid) were used in the ESI mode to compare their effectiveness. The results in Figure 13 show that, in general, the peak intensities are comparable among three modifiers. However, the elution order of the peak Mexacarbate (as well as Aminocarb) was different. Therefore, a single selected-ion-monitoring (SIM) method should not be used for different modifiers.

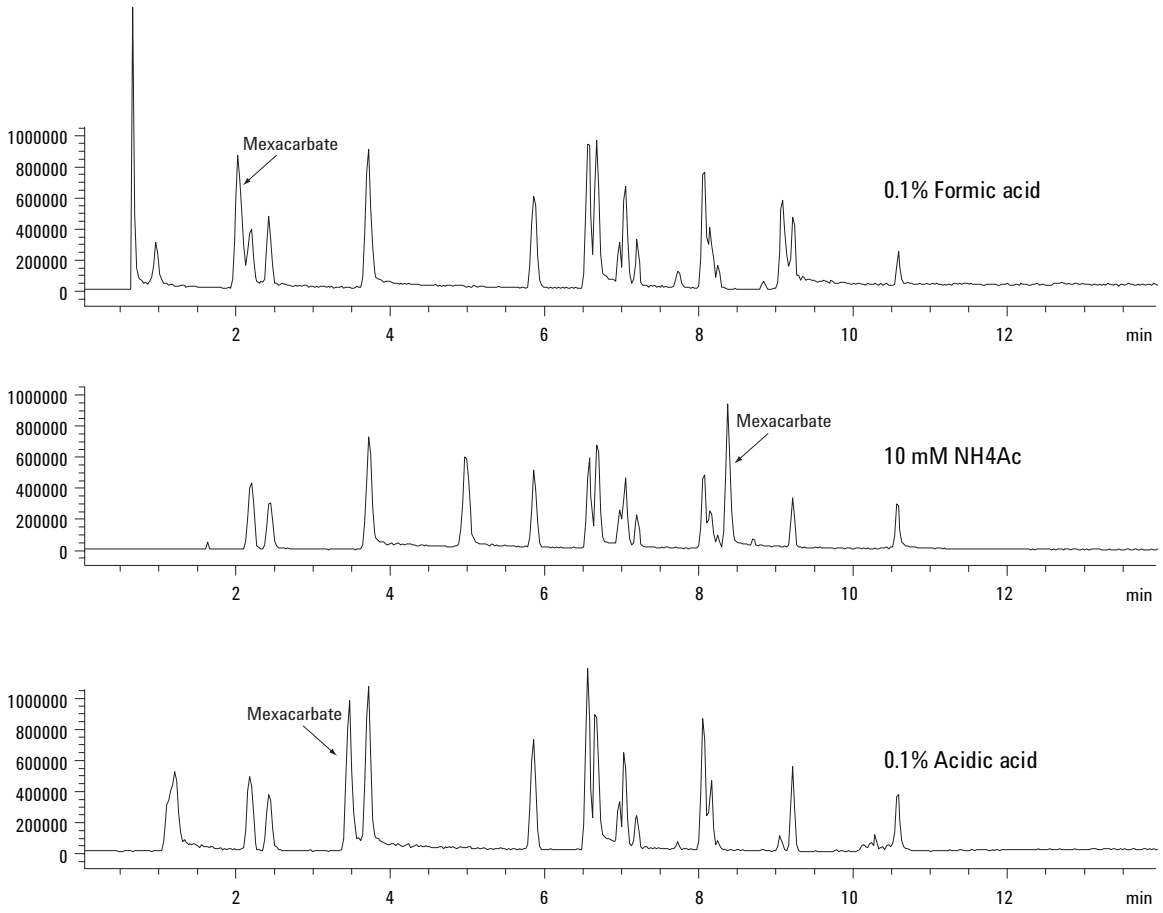


Figure 13. Different modifiers in ESI resulted in comparable peak intensities but changed the peak elution order.

Conclusions

Carbamates and phenyl ureas were successfully analyzed using ESI, APCI, and APPI sources. APPI and APCI have lower background signals and fewer background peaks than ESI. The results show that carbamates, in general, give better S/N from ESI than from APCI or APPI. However, it is just the opposite for phenyl ureas, for example, the S/N is better from APCI or APPI than from ESI. A small amount of post-column acetone was needed in the APPI source as a dopant. The dopant is photoionizable and is used to transfer charge to the analyte.

The typical ESI quantitation limit for these compounds is 20 pg on column using SIM. Some carbamates and phenyl ureas (for example, Propoxur, Carbofuran, and Siduron) exhibited protonated and sodiated dimers in the full scan ESI spectra.

References

1. "Basics of LC/MS," Agilent Technologies Primer, Publication 5988-2045EN, February 15, 2001.
2. "PhotoMate Atmospheric Pressure Photoionization Source from Syagen Technology," Agilent Technologies Brochure, Publication 5988-3130EN, May 25, 2001.

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