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A Prescription for Rapid Analyses: Gas Chromatography with Time-of-Flight Mass Spectrometry Detection

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Abstract

An increase in sample throughput for GC/MS is attained using shorter, smaller bore columns and higher linear flow rates. In recognition of the need for faster MS detection, TOFMS with time array detection is used. The combination of faster GC and faster MS results in a decrease of over $10\times$ for the analysis of pesticide and herbicide mixtures. The greater data density generated at 50 spectra/sec and the lack of spectral skewing enable rapid, effective deconvolution where peaks co-elute, thereby maintaining analytical integrity throughout the entire analysis.

Introduction

An interesting paradox exists in the field of environmental analysis. The large number and many types of compounds that need to be analyzed and the vast number of locations to be monitored, when combined with the fact that most of the analytes measured exhibit dynamic, time-dependent behavior, often result in an undersampling that challenges the statistical veracity of the analytical results. In spite of this undersampling, there still exists a considerable sample glut which taxes the resources available for these analyses. This situation can be remedied in three ways: more resources being made available, an unlikely situation when considering the present mood of business and government; the development of new novel methods and techniques which are inherently faster, yielding higher throughput; or improvements in the throughput of existing technologies. This study concerns the latter, namely gas chromatography/mass spectrometry (GC/MS), which is well established as the preferred analytical tool for volatile and semi-volatile analyte mixtures.

The speed of GC separations can be greatly increased by use of shorter length, smaller bore columns and high linear carrier gas flow rates. While decreasing the diameter increases the theoretical resolution, the short column length and high flow rate inevitably result in minimal temporal separation of the analytes. Furthermore, the eluant peak widths are typically narrow, often extending into the sub-second region. Under these conditions, 20 or more spectra/sec are required for quantitative purposes and higher acquisition rates are essential for the deconvolution of co-eluting peaks. The only mass spectrometers capable of these spectral acquisition rates are array detectors¹ and, of these, the only commercial unit presently capable of attaining these speeds with adequate sensitivity is the time-of flight mass spectrometer using time array detection² (TOFMS-TAD). This work describes efforts using high speed chromatography and TOFMS-TAD that significantly increase productivity in the analysis of pesticides and herbicides.

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Experimental Method

An 13-component herbicide mixture was obtained from Supelco. Separation of the analytes was performed on a Hewlett Packard 6890 gas chromatograph with a 3 m Rtx-5 column (0.1 mm I.D., 0.10 μ m film thickness) using a 100:1 split injection of a 1.0 μ L sample volume. The oven temperature was ramped from 90 300 C at the chromatograph's maximum rate (120 C/min nominal). The He carrier gas linear velocity was set at 100 cm/sec and pressure programming was used to ensure constant velocity throughout the analysis. Electron impact mass spectral data were acquired using a LECO FCD-650 time-of-flight mass spectrometer equipped with an integrating transient recorder. Ion source sampling occurred at 5000 Hz with a spectral generation rate of 50 spectra/sec. The mass range was m/z 40 450.

Results and Discussion

A reconstructed total ion chromatogram representing the 2 minute analysis of the herbicide mixture is illustrated in Figure 1. The typical chromatographic time required using conventional chromatographic techniques requires 20 minutes or more. While several compounds exhibited considerable chromatographic overlap as shown in Figure 2, pure mass spectra of the individual compounds were obtained using mathematical deconvolution (Figure 3). The spectra obtained agree closely with those obtained using isolated reference standards and with reference spectra found in the National Institutes of Standards and Technology mass spectral database.

The use of TOFMS detection provides increased analytical power for GC/MS analyses. In addition to the speed of spectral generation, two other advantages are gained with this instrumentation. Time array detection by integrating transient recording utilizes all of the ions striking the detector subsequent to each and every ion source extraction. This provides excellent detectability (typically picogram levels) at the high spectral generation rates and the extraction of all ions simultaneously produces fragmentation patterns that are devoid of any skewing due to the dynamics of the chromatography. This makes mathematical deconvolution rapid and effective even for minor sample components. Due to this lack of skewing, the readily recoverable mass spectrum for each compound is library matchable with excellent correlation. What is sacrificed with this approach is a decrease in the dynamic range. However, if increases in throughput are significantly large, as is the case with these results, repeated runs using differing concentrations can readily be accommodated when necessary.

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Figure 2: Reconstructed total ion chromatogram (RTIC) and normalized chromatograms of two co-eluting herbicide analytes.

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Figure 3: Deconvoluted mass spectra of the co-eluting analytes illustrated in Figure 2.

Literature Cited

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