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Gas chromatography–vacuum ultraviolet spectroscopy for multiclass pesticide identification☆

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ABSTRACT

A new vacuum ultraviolet detector for gas chromatography was recently developed and applied to multiclass pesticide identification. VUV detection features full spectral acquisition in a wavelength range of 115–240 nm, where virtually all chemical species absorb. VUV absorption spectra of 37 pesticides across different classes were recorded. These pesticides display rich gas phase absorption features across various classes. Even for isomeric compounds, such as hexachlorocyclohexane (HCH) isomers, the VUV absorption spectra are unique and can be easily differentiated. Also demonstrated is the ability to use VUV data analysis software for deconvolution of co-eluting signals. As a universal detector, VUV provides both qualitative and quantitative information. It offers high specificity, sensitivity (pg on-column detection limits), and a fast data acquisition rate, making it a powerful tool for multiclass pesticide screening when combined with gas chromatography.

1. Introduction

Pesticides are the most highly regulated chemicals, which include insecticides, herbicides, fungicides, and various other substances used to control pests. Under United States law, a pesticide is also any substance or mixture of substances intended for use as a plant regulator, defoliant, or desiccant [1]. The 2005 FDA Glossary of Pesticide Chemicals contains entries for 1045 chemicals [2]; structurally, they contain myriad different heteroatoms and multiple functional groups. Much effort has been placed on the development of analytical methods, which can simultaneously determine multiple classes of pesticides in a single analytical run.

Currently, liquid chromatography and gas chromatography coupled with tandem mass spectrometry (LC–MS/MS and GC–MS/MS) and operated under selected reaction monitoring (SRM) mode are the most commonly used targeted pesticide screening techniques [3–7]. Despite their high speed and sensitivity, GC–MS/MS and LC–MS/MS are limited in certain applications. For example, matrices used in pesticide analysis are usually complex. Isobaric matrix interferences with the same mass as the pesticides, but different molecular formula, are commonly present. In cases where multiple isomers of a pesticide are present in the sample, unit resolution MS often fails to differentiate these compounds; false positive or false negative results are a major concern. Mass analyzers with higher resolving power and full chromatographic resolution of analytes are often necessary in these applications [8,9]. In other cases where analytes of interest degrade rapidly during ionization (e.g., N-trihalomethylthio fungicides [10,11]), MS becomes unsuitable.

A vacuum ultraviolet (VUV) detector has been recently developed, and it is able to address many of the limitations for pesticide analysis discussed above [12]. The VUV detector provides rapid measurement of absorption spectra from 115 to 240 nm, where essentially all chemical species absorb. Absorption spectra for a variety of small molecules collected using GC–VUV show unique and rich features. Even isomers of xylenes and naphthol, which are difficult to resolve chromatographically and have identical mass spectra, were easily differentiated based on their absorption profiles. Data analysis software used in GC–VUV can deconvolve co-eluting signals based on matching measured signals to library reference spectra. Since no ionization is needed, VUV can also be used to analyze labile compounds that cannot be analyzed by MS. Fast data acquisition rate (up to 100 Hz) makes VUV compatible with fast GC applications. Quantitation follows standard Beer–Lambert law principles, and the absolute amount (i.e., the number of molecules) in the detector flow cell can be determined if

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an absorption cross-section for the chemical compound is known. In the initial report on GC–VUV [8], a detection limit of 186 pg on-column was reported for captan, an N-triohalomethylthio fungicide, which is not easily detectable using GC–MS.

The aim of this study was to demonstrate the capabilities of VUV as a universal GC detector for multiclass pesticide determination. VUV absorption spectra of selected pesticides, including organochlorine, organophosphate, carbamate, and pyrethroid compounds were collected and evaluated. Special attention was given to demonstrating the ability of the detector to deconvolute the contribution of multiple components to signals obtained from co-eluting compounds. VUV spectroscopy also provided sensitive quantitative analysis.

2. Theory and VUV detector hardware

The wavelength range of VUV electromagnetic radiation is defined as 10–200 nm. High energy electronic transitions (e.g., $\sigma \rightarrow \sigma^*$, $n \rightarrow \pi^*$, and $\pi \rightarrow \pi^*$) are probed by absorption of light by bonded and nonbonded electrons in this region. Bench top analytical measurements in this wavelength range have only been a recent development, due to a lack of convenient light sources that emit continuous and high intensity radiation, and detectors that generate linear signal responses in the VUV region [12–16]. Previous VUV absorption spectral measurements were restricted to synchrotron facilities [17–20]. In other cases, where ultraviolet absorption detectors for gas chromatography were demonstrated in the past, the measurements were limited to a single wavelength [14] (no qualitative information) or a wavelength range above 168 nm with limited signal-to-noise performance at short wavelengths [15,16].

A general schematic of the VUV instrument arrangement and operation principles of the GC–VUV instrument can be found in a previous article [12]. The VUV detector can be connected to any standard GC system through a heated transfer line (owned by the VUV detector), which contains a deactivated stainless steel capillary that is thermally insulated. Compounds that elute from the GC column enter the heated transfer line, and then the flow cell where they absorb UV light and then exit the flow cell through the exit vent. A makeup gas line, which delivers argon or nitrogen, tees into the flow cell (10 cm path length; 80 μl cell volume). The flow rate of this makeup gas can be adjusted to alter residence time of the analyte in the flow cell, and to optimize the sensitivity. For higher concentration analytes, a higher makeup flow is adopted to avoid detector saturation. Conversely, a lower makeup flow can be used to enhance the sensitivity of weaker absorbing (or lower concentration) species by allowing more molecules to be detected per unit time. Incorporating makeup gas into the flow cell also eliminates potential band broadening caused by the long path length. The ideal makeup pressure setting is a balance between applying enough makeup gas to minimize broadening while maintaining a sufficient residence time to achieve detection limits required by the application. A high makeup flow may also be used to purge the detector in the event of flow cell contamination. A deuterium lamp is used as the light source, and a back-thinned charge-coupled device collects full spectrum measurements from 115 to 240 nm at an acquisition rate as high as 100 Hz. A dark and background scan is collected at the beginning of each run for background subtraction. A common misconception is that vacuum pumps are needed to operate the detector. Historically, pumps were used to prevent oxygen and moisture contamination, hence the name VUV. The source module, flow cell, and detector module of the VGA-100 system, however, are specially engineered to prevent such contamination from occurring.

3. Material and methods

VUV absorption spectra for a total of 38 pesticide standards (Cerilliant, Round Rock, Texas) were recorded on a VGA-100 VUV detector (VUV Analytics, Inc., Austin, TX), which was coupled to a Shimadzu GC-2010 gas chromatograph (Shimadzu Scientific Instrument, Inc., Columbia, MD). These standards were purchased as three separate pre-prepared mixtures. A list of all pesticides and their structures is provided in Table 1. The concentration of these standards varied from 400 to 2000 μg/ml. The standards were diluted to working concentrations between 40 and 200 μg/ml in dichloromethane (ACS reagent, 99.6%, Aldrich Chemical Co., Inc., Milwaukee, WI). Columns include a HP-5ms column (30 m × 250 μm i.d. × 0.25 μm d_f) (Agilent Technology Inc., Santa Clara, CA) and a ZB-5 (15 m × 250 μm i.d. × 0.25 μm d_f) (Phenomenex Inc., Torrance, CA). A Shimadzu AOC-20i Auto Injector was used to inject 0.5 μl of sample. The temperature of the GC injector was 250 °C. The temperature of the VUV transfer line and the flow cell was 300 and 275 °C, respectively. The pressure of makeup gas was set to 0.25 psi throughout the experiments, except for limits of detection (LOD) determinations for which it was set to 0.1 psi. Helium was used as the GC carrier gas.

Preliminary, LOD were determined for dieldrin and p,p'-DDE standards and reported as mass on-column that generated a signal-to-noise ratio (S/N) equal to three. Absorption was integrated across specific spectral ranges that yielded optimal detector S/N.

4. Results and discussion

4.1. VUV spectral features

In solution phase absorption analysis, spectral broadening caused by interactions between target molecules and surrounding solvent often results in featureless absorption spectra. Without the blurring effects induced by the solvent, gas phase absorption spectra show more features that are highly sensitive to the structure of the molecule.

VUV absorption spectra of the 38 pesticides showed rich features (see the electronic supplementary information document for complete spectra of all pesticide analytes). Within each class, different pesticides displayed distinctive absorption spectra. Fig. 1 shows VUV spectra of four organophosphate pesticides (i.e., sulfotep, phorate, methyl parathion, and famphur). Compounds with aromatic structure were observed to absorb strongly in the 160–200 nm region, whereas nonaromatic molecules absorb less intensively in this region. This feature can be valuable in differentiating aromatic pesticides from other pesticides, and increased sensitivity for different pesticide classes can be realized by integrating the absorbance response in selected wavelength ranges where it is highest. This is demonstrated in Fig. 2, where the absorbance response for a total of 20 semi-volatile pesticides was integrated in 125–240 nm (green trace), and in 170–200 nm (red trace) where aromatic pesticides absorb strongly (Fig. 1C and D). Among these pesticides, four contain aromatic structure (i.e., methoxychlor, p,p'-DDD, p,p'-DDE, and p,p'-DDT) and can be easily distinguished from the ones that lack aromaticity by comparing the intensity of absorbance integrated in these two regions. It is also clear that integration within certain wavelength windows can be critical in VUV quantitative analysis.

Preliminarily, data showed the detector LOD for dieldrin and p,p'-DDE in neat solution were approximately 500 and 125 pg on-column, respectively. These LODs would vary in real applications depending on factors such as sample preparation. The difference in LOD between dieldrin and p,p'-DDE was expected, because p,p'-DDE contains aromatic rings and absorbs strongly in the