Application Note

Permanent Gas Analysis by Gas Chromatography – Vacuum Ultraviolet Spectroscopy

Introduction

Gas Chromatography (GC) is a mature analytical technology used predominately for separating and quantifying the components of complex organic chemical mixtures. A wide range of columns and sample introduction techniques allow GC to be applied to most analytical problems involving volatile and semi-volatile compounds. One such application is the analysis of permanent gases, which are compounds that do not liquefy under ambient conditions (e.g., oxygen and carbon monoxide). The analytical detection of these gases is of great interest in environmental, petrochemical, chemical, and energy industries.

Natural gas, for instance, is comprised of a number of permanent gases including methane, its largest component, as well as lesser amounts of carbon dioxide, nitrogen, hydrogen sulfide, and length C5-C10 hydrocarbons. Natural gas comes from two distinct sources, the decomposition of biomass (biogenic) or geological processes (thermogenic). While biogenic gas is primarily methane, thermogenic gas is created under extreme temperature and pressures and this results in the presence of C2-C4 hydrocarbons. Analysis for compositional differences can be used to distinguish between the two sources.

In addition to environmental applications like drinking water contamination, permanent gas analysis is also relevant in the assessment of lithium-ion and lithium-metal batteries. These batteries, which have become nearly ubiquitous, are susceptible to thermal runaway reactions which can generate substantial amounts of toxic and flammable gases. As these events represent major environmental health hazards, there is a need for the precise determination of these gases. Only then can risk factors be properly assessed.

The GC separation of permanent gases can be achieved through the use of common technology like porous-layer open tubular (PLOT) columns; however, detection is not always so straightforward. The most common GC detection methods including flame ionization (FID), electron capture (ECD), thermal conductivity (TCD), and mass spectrometry (MSD). Each of these detection methods has clear analytical drawbacks. FID and ECD, for example, are only capable of detecting carbon-containing and halogenated compounds, respectively. And while TCD does offer universal detection, it exhibits poor sensitivity and is therefore unsuitable for the analysis of trace gases. Finally, MSD encounters significant limitations in the detection of low mass compounds which are typically encountered in permanent gas analysis.

To address these known limitations and to additionally bolster the capabilities of GC analysis, a new type of detector based on absorption spectroscopy in the vacuum ultraviolet (VUV) region (120nm – 240nm) of the electromagnetic spectrum has been recently developed[1]. While previously limited to bright source synchrotron facilities, recent scientific advances have unlocked this valuable spectral domain where most compounds absorb strongly and exhibit highly-featured, unique spectra even for isomeric species. These characteristic spectra are useful for orthogonal identification as well as quantitation of chemical species. Additionally, VUV spectroscopy deconvolution algorithms allow for straightforward deconvolution of co-eluting species.

The VGA-100 VUV detector (schematic shown in Figure 1) is the very first bench-top spectrometer capable of full VUV spectrum detection, and can be connected to any standard GC through a heated transfer line. In this paper, we demonstrate the use of the VGA-100 in several permanent gas applications including the analysis of 1) natural gas in the headspace of collected groundwaters and 2) evolved gases from thermal runaway events in Li-ion and Li-metal batteries. The VGA-100 is shown to

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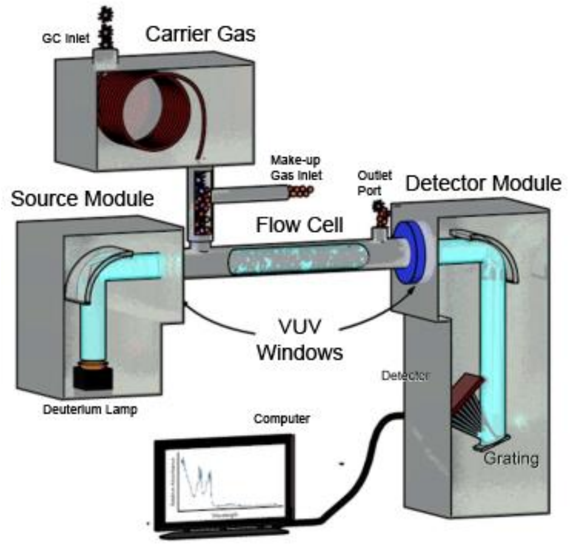

Figure 1. Schematic (not to scale) of the GC-VUV instrument. Dimensions are 13 in. (w) x 30 in. (d) x 17 in. (h). Flow cell volume is ~80 µL. Path length is 10 cm.

provide reliable detection of permanent gases in these applications.

Experimental

- Standards and Samples

A natural gas standard containing nitrogen, carbon dioxide, methane, ethane, propane, iso-butane, *n*-butane, *iso*-pentane, *n*-pentane, and hexanes+EX6 was obtained from DCG Partnership.

Water samples containing natural gas were collected from the Barnett Shale formation in Parker County, Texas. These samples were obtained from water wells located less than one mile from the site of gas wells using hydraulic fracturing (i.e., 'fracking'). Samples were purged of all bubbles before refrigerator storage. Just before analysis, samples were vortexed thoroughly and sonicated for 10s, then allowed to equilibrate to room temperature. A 0.300 mL headspace volume was injected into the GC-VUV using a 1 mL Pressure-Lok VICI gas tight syringe.

Li-ion and Li-metal battery samples were obtained commercially and included lithium-cobalt-oxide (CO), lithium-nickel-manganese-cobalt-oxide (NMCO), and lithium-manganese-nickel (MN) 18650 cells. A thermal event was induced by heating tape and gaseous byproducts were collected using multi-layer foil gas sampling bags in a specially designed chamber. A 0.500 mL volume of gas was withdrawn and injected into the GC-VUV.

- GC Separation/Detection

A Shimadzu GC-2010 gas chromatograph coupled with a VUV Analytics VGA-100 VUV gas detector was used throughout. Separation was achieved using an HP PLOT/Q (30 m x 0.32 mm x 20 µm) from Agilent Technologies operated in constant velocity mode (27 cm/s) with helium carrier gas. The transfer line and flow cell temperatures were fixed at 300 °C and 275 °C, respectively, with a make-up gas (argon) set to 0.25 psi. VUV spectra were collected at a rate of 10 Hz.

Injections were performed with the injection port set exclusively at 250 °C. The oven profile for natural gas analysis began at 50 °C (held for 4 min) followed by an increase to 200 °C at a rate of 15 °C/min (held for 5 min). A split ratio of 20:1 was used. For the analysis of Li battery off-gassing, the oven profile was set to start at 40 °C (held for 7.85 min) and then ramped to 250 °C at a rate of 5.7 °C/min (held for 7 min). The injection port here was operated with a split ratio of 5:1.

Results and Discussion

- Analysis of natural gas standard

The GC analysis of natural gas has customarily been performed with both TCD and FID detection, with TCD to measure nitrogen, carbon dioxide and light hydrocarbons, and FID for the determination of heavier hydrocarbons. However, using GC-VUV it is possible to analyze all of these components in a single run with a single detector. Figure 2A presents the chromatographic separation of a natural gas standard with 125-240 nm detection. Peak intensities in this chromatogram are derived from the average absorbance across the full wavelength range, however each peak has its own associated absorption spectra as seen in Figures 2B and 2C. The variety in spectral features shown here are very useful for identification purposes; methane, for example, can be differentiated from longer *n*-alkanes based on the difference in spectral response in the 125-150 nm region. Individual components were identified through the use of VUV spectral library matching, which was automated by a pattern recognition algorithm in the VUV software.

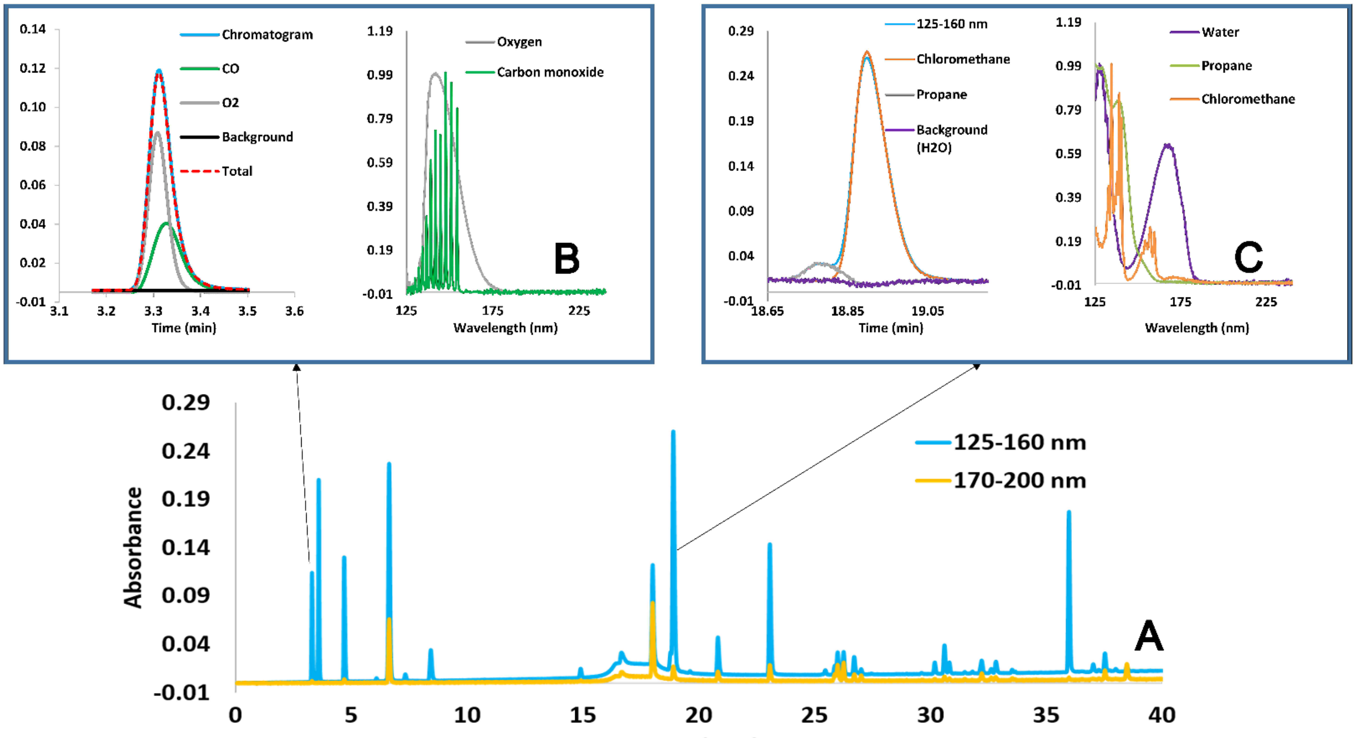

Figure 2. GC-VUV chromatogram from a natural gas standard (A), with selected spectra of hydrocarbon (B) and other (C) components. 125-240 nm detection.

- ➢ Analysis of natural gas in water

Drinking-water wells contaminated with methane are frequently analyzed to determine the source of contamination – namely whether it is of thermogenic or biogenic origin. It is thermogenic, not biogenic, methane that is targeted in natural gas extraction via hydraulic fracturing. Understanding the origin of the methane is therefore crucial for identifying the source of contamination. The presence or absence of C2-C4 hydrocarbons provides the means to differentiate the two types.

Figure 3 displays chromatograms from the GC-VUV analysis of the headspace of three water samples collected near fracking sites. These results demonstrate that the headspace samples are very similar in composition to the natural gas standard (Figure 2). The most notable difference is the abundance of water in the headspace, which is to be expected. The presence of C2-C4 hydrocarbon peaks in these chromatograms confirms that the water has been contaminated by natural gas of thermogenic origin. Quantitation of the headspace components could be achieved with appropriate standards, but is beyond the scope of this work.

- ➢ Analysis of products from thermal decomposition of Li-ion and Li-metal batteries

GC-VUV chromatograms of the thermally evolved gases were collected for each of the Li-ion and Li-metal battery types. Each battery generated significant quantities of volatile gases, including those that are flammable (e.g., methane, ethylene, and propene) and toxic (e.g., acetaldehyde, 1,3-butadiene, and chloromethane). Identification was once again made possible by VUV spectral library matching. The resulting chromatograms displayed generally good resolution following separation on the PLOT column, however there were a few occurrences of co-elution.

One such occurrence of co-elution was the oxygen/carbon monoxide peak with a retention time of approximately 3.3 minutes. These two species are key decomposition products in the study of thermal runaway reactions of Li-ion batteries, but unfortunately they are not easily resolved on PLOT/Q columns. MS detection is likewise incapable of resolving these co-eluting peaks into their relative contributions. In order to address this issue, alternative column technologies with stronger adsorption mechanisms must normally be employed, which then results in excessive retention of the remaining components. The VGA-100 detector and software provide

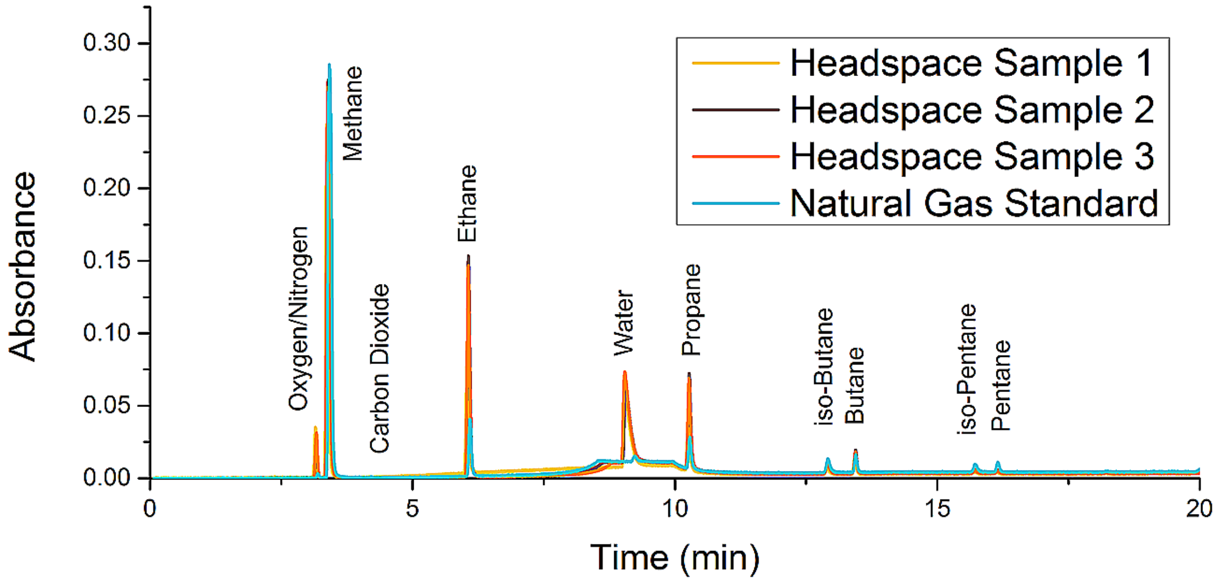

Figure 3. Overlaid GC-VUV chromatograms of water headspace samples and a natural gas clear **standard. 125-240 nm detection.**

the means for the deconvolution of spectrally distinct, co-eluting species.

Successful deconvolution of the oxygen and carbon monoxide chromatographic signals is presented in Figure 4 for the NMCO battery sample. A magnified view of these co-eluted peaks in the NMCO chromatogram is shown in Figure 4A. Figure 4B then displays the VUV absorption spectrum observed at the chromatographic peak maximum (labeled: 'Original') as well as the individual VUV spectra for oxygen and carbon monoxide. There is a contrast in these two spectra – while the oxygen spectrum consists largely of one broad hump spanning 130-175 nm, the carbon monoxide spectrum possesses numerous sharp vibrational features in this same range. This marked difference in the spectral responses of the two species enables their efficient deconvolution. Thus, the 'Original' spectral response is readily decoupled into relative contributions of oxygen and carbon monoxide, which the VGA-100 software then uses to construct a deconvolved chromatographic response (Figure 4A).

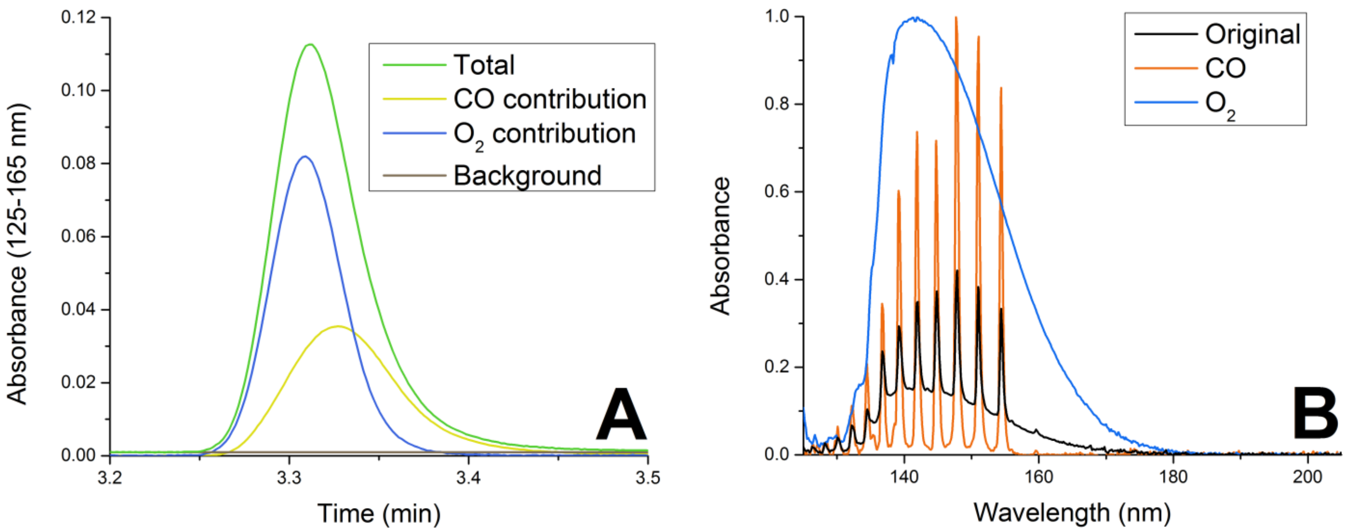

Figure 4. Deconvolution of co-eluting CO and O_2 chromatographic peaks from the off-gassing of the NMCO battery sample (A) using the distinct VUV spectral contributions obtained at 3.30 min (B).

Conclusion

A new, commercially available VUV wavelength detector, the VGA-100, was applied to the separation and analysis of permanent gas mixtures. The detector's universal detection and identification capabilities provide a superior analytical assay compared to existing technologies. In the analysis of groundwaters near fracking sites, water samples were shown to be contaminated with natural gas of thermogenic origin. The VGA-100 was likewise able to detect and identify gases evolved from thermal runaway events of Li-ion and Li-metal batteries. Overlapping chromatographic peaks from these samples were successfully decoupled through a unique deconvolution process made possible through the use VUV spectroscopy. The VGA-100 provides a worthy alternative for permanent gas analysis.

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