Permanent gas analysis using gas chromatography with vacuum ultraviolet detection☆

Ling Bai[a], Jonathan Smuts[b], Phillip Walsh[b], Hui Fan[a], Zacariah Hildenbrand[c], Derek Wong[d], David Wetz[d], Kevin A. Schug[a,*]

[a] Department of Chemistry and Biochemistry, The University of Texas at Arlington, Arlington, TX, United States
[b] VUV Analytics, Inc., Austin, TX, United States
[c] Inform Environmental, LLC, Dallas, TX, United States
[d] Department of Electrical Engineering, The University of Texas at Arlington, Arlington, TX, United States

ABSTRACT

The analysis of complex mixtures of permanent gases consisting of low molecular weight hydrocarbons, inert gases, and toxic species plays an increasingly important role in today's economy. A new gas chromatography detector based on vacuum ultraviolet (VUV) spectroscopy (GC–VUV), which simultaneously collects full scan (115–240 nm) VUV and UV absorption of eluting analytes, was applied to analyze mixtures of permanent gases. Sample mixtures ranged from off-gassing of decomposing Li-ion and Li-metal batteries to natural gas samples and water samples taken from private wells in close proximity to unconventional natural gas extraction. Gas chromatography separations were performed with a porous layer open tubular column. Components such as C1–C5 linear and branched hydrocarbons, water, oxygen, and nitrogen were separated and detected in natural gas and the headspace of natural gas-contaminated water samples. Of interest for the transport of lithium batteries were the detection of flammable and toxic gases, such as methane, ethylene, chloromethane, dimethyl ether, 1,3-butadiene, CS_2, and methylpropionate, among others. Featured is the capability for deconvolution of co-eluting signals from different analytes.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Permanent gases, those chemical compounds that do not liquefy under ambient conditions, are of great interest in the petrochemical, chemical, and energy industries [1]. Natural gas has emerged as a versatile source of energy in the past decade. As a highly traded international valuable commodity, there is a significant demand for natural gas analysis. Natural gas mainly contains methane, but also ethane, propane, and other minor constituents such as carbon dioxide, hydrogen sulfide, nitrogen, and longer hydrocarbons, ranging from C6 to C10. Purified natural gas is odorless and colorless, but sometimes odorants are added for safety and leak detection [2].

Increased natural gas extraction based on directional drilling and hydraulic fracturing stimulation technologies has generated concerns about the contamination of drinking water and other environmental problems. Methane has limited solubility in water and can be flammable when vented to the atmosphere. Prior research has shown instances of very high methane concentrations in water. Some were 17 times higher on average in shallow water wells near active drilling and extraction areas than in wells from non-active areas in northeastern Pennsylvania and upstate New York. Such concentration levels are considered hazardous; determining the source of the methane is therefore important in order to devise mitigation strategies [3,4]. Additionally, permanent gases, like methane (CH_4), nitrous oxide (N_2O), and carbon dioxide (CO_2) are primary contributors to climate change [5]. Small leakages of methane, the major component of natural gas, have been indicated to have greater global warming potential than previously believed, when the indirect influence of methane on atmospheric aerosols are considered [6].

There are two different types of methane produced naturally – biogenic methane and thermogenic methane. Biogenic methane is produced at shallow depths as a byproduct of bacterial metabolism. Thermogenic methane is formed by geological processes at depths exceeding 1000 m as a function of high temperature and pressure.

In the latter, the decomposition of organic materials into methane gas and heavier saturated components (C2–C4 hydrocarbons) creates a signature that can be used to discern between thermogenic and biogenic sources. Thermogenic methane is also the primary target of unconventional natural gas extraction.

The determination of hazardous decomposition products from a thermal runaway reaction of lithium-ion and lithium-metal batteries is another important gas analysis application [7]. This is highlighted by the near ubiquitous use of lithium-ion batteries in cell phones, laptops, automobiles, and other portable devices [8]. The chemistry in Li-ion batteries is designed to provide maximum energy density, which is susceptible to thermal runaway when overheated from overcharging or exposed to high temperatures. The decomposition of the anode and cathode results in battery capacity loss and environmental hazards. During transportation of Li-ion batteries, it is possible for an internal short to form, a battery to rupture, for toxic and flammable gases to form, and even a fire to begin. The amount of gas generated can be substantial and can cause very hazardous environmental or health problems. Undesired decomposition from both capacity loss and gas evolution should be carefully analyzed and controlled [9].

At the current pace, lithium demand is expected to increase 18-fold from 165,000 tons per year in 2013 to a minimum of 3 Mt (million tons) per year by 2030 [10]. The global lithium resource is estimated to be about 39 Mt for the period 2010–2100. The high growth rate regarding the production and use of lithium has attracted attention about assessment of environmental and safety concerns. In May 1999, the International Power Sources Symposium proposed an amendment about transportation of dangerous goods – lithium-ion batteries. Concerns regarding the transportation of lithium-ion batteries have since appeared in more regulations [11]. Many fires and explosions have been reported throughout the world during the past years. The flammability of the electrolyte, the rate of charge and/or discharge, and the engineering of the battery pack provide various levels of concern. In some cases, greater instability is accepted as a consequence of higher performance products [12]. These risk factors need to be assessed.

Gas chromatography has continuously played an important role in gas analysis [13]. Good selectivity and sensitivity of separation is tightly related to column chemistries, sample introduction techniques, and detectors [14]. Porous-layer open tubular (PLOT) columns, first suggested by Golay in the late 1950s, are used in many contemporary applications of GC, and are considered to be a worthy alternative to packed columns for gas analysis. Compared to packed columns, PLOT columns provide better efficiency, greater resolution, and faster separations; collectively, these have extended their application to a wide range of fixed gases, light hydrocarbons, and volatile solvents [15]. Additionally, compared with the most common liquid stationary phase wall-coated open tubular (WCOT) columns, PLOT columns exhibit more retention of volatile compounds and permanent gases at sub-ambient and super-ambient oven temperatures, and thus facilitate better qualitative and quantitative abilities for these analytes [16].

Over 60 detectors have been designed for GC application since the inception of the technique. These include the well-known flame ionization detector (FID), thermal conductivity detector (TCD), electron capture detector (ECD), and mass spectrometer detector (MSD). However, not all of them are suitable for the analysis of permanent gases or highly volatile compounds. FID and ECD are considered as selective detectors that only detect compounds with specific chemical, physical, and molecular properties. For example, while FID provides high sensitivity and wide linear range, it only detects carbon-containing compounds. ECD only detects compounds with high electron affinity, therefore it is often used for selective detection of halogenated compounds. TCD, on the other hand, is a universal detector; however, the sensitivity of the TCD

is generally orders of magnitude worse than other detectors [17]. Even though many official standardized methods rely on MSD technology, because of its excellent sensitivity for trace quantitative analysis and capability for identification of analytes of interest, it has significant limitations for the detection of low mass compounds typically encountered in gas analysis.

To address these limitations, a vacuum ultraviolet (VUV) detector has been recently introduced [14]. Gas chromatography with VUV detection (GC–VUV), has been presented as an alternative tool for GC–MS, and it has been demonstrated for the analysis of hydrocarbons, polyaromatic hydrocarbons, fatty acids, pesticides, drugs, and estrogens. GC–VUV provides universal detection through full wavelength range absorption measurements in the 115–240 nm range. All chemical compounds absorb in this wavelength region and have unique and highly featured absorption spectra. Analytes eluting from the GC are passed through a heated transfer line, mixed with a make-up gas, and enter the flow cell (10 cm path length; 80 μL volume). The make-up gas flow can be varied to optimize residence time in the cell, and to minimize band broadening. The absorption of VUV light, provided with a deuterium source module, is monitored using a charge coupled detector at a rate of up to 100 Hz.

The aim of this study is to demonstrate the use of GC–VUV for analysis of permanent gases from sources of high relevance to the modern world and energy industry. Included are applications to natural gas characterization, the analysis of natural gas in the headspace of collected groundwater, and the evolution of gases from thermal runaway events in Li-ion and Li-metal batteries. GC–VUV is shown here to provide reliable detection of gaseous (and other volatile/semi-volatile) components in these applications. The detector can be used to fully deconvolute co-eluting species based on known absorption cross-sections for the different analytes.

2. Experimental

2.1. Instrumentation

A Shimadzu GC-2010 gas chromatograph (Shimadzu Scientific Instruments, Inc., Columbia MD) was coupled to a VGA-100 VUV detector (VUV Analytics, Inc., Austin TX) and used to collect data from a variety of gas samples. The data collection rate was set at 10 Hz. The transfer line and flow cell temperatures were set at 300 °C and 275 °C, respectively, and the make-up gas (argon) was set to 0.25 psi. While make-up gas reduces the residence time of the analyte in the flow cell and thus its signal, we found that a set pressure of 0.25 psi was appropriate for this application. The make-up gas pressure is used to optimize residence time of the peak in the flow for sufficient signal averaging. The column used was an HP PLOT/Q (30 m × 0.32 mm × 20 μm) from Agilent Technologies (Santa Clara, CA) and it was operated in the constant velocity mode (27 cm s^{-1}) with helium carrier gas.

The oven profile for natural gas application was set to start at 50 °C (held for 4 min) and then increased to 200 °C at a rate of 15 °C/min (held for 5 min). The injection port was operated with a split ratio of 20:1. The oven profile for Li battery off-gassing applications was set to start at 40 °C (held for 7.85 min) and then increased to 250 °C at a rate of 5.7 °C/min (held for 7 min). The injection port was operated with a split ratio of 5:1. The injection port temperature was set at 250 °C. Manual injection was performed. The injection volume varied depending on application.

2.2. Natural gas standard

A natural gas standard containing nitrogen, carbon dioxide, methane, ethane, propane, *iso*-butane, *n*-butane, *iso*-pentane,