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Evolved gas composition monitoring by repetitive injection gas chromatography

Robert L. White*

Department of Chemistry & Biochemistry, University of Oklahoma, Norman, OK 73069, USA

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ABSTRACT

Performance characteristics and applications of a small volume gas chromatograph oven are described. Heating and cooling properties of the apparatus are evaluated and examples are given illustrating the advantages of greatly reducing the air bath volume surrounding fused silica columns. Fast heating and cooling of the oven permit it to be employed for repetitive injection analyses. By using fast gas chromatography separations to achieve short assay cycle times, the apparatus can be employed for on-line species-specific gas stream composition monitoring when volatile species concentrations vary on time scales of a few minutes or longer. This capability facilitates repeated sampling and fast gas chromatographic separations of volatile product mixtures produced during thermal analyses. Applications of repetitive injection gas chromatography–mass spectrometry evolved gas analyses to monitoring purge gas effluent streams containing volatile acid catalyzed polymer cracking products are described. The influence of thermal analysis and chromatographic experimental parameters on effluent sampling frequency are delineated.

1. Introduction

Most laboratory gas chromatography (GC) instruments were designed with flexible configurations. These instruments often have multiple injector and detector ports in order to support different operating modes. Large oven volumes facilitate the use of a wide range of separating columns. However, the most efficient gas chromatography separations are achieved with small diameter fused silica columns, which do not require large ovens for heating [1].

The tradeoffs between gas chromatographic separation efficiency and analysis time are well known [2–10]. Faster gas chromatographic separations are possible when a separation method provides more resolution than is needed to isolate mixture components. For these instances, separation methods can often be modified to permit faster analyses by sacrificing excess chromatographic resolution [5]. For mixtures containing species with widely varying retention properties, separations often require heating the column with a temperature ramp. Unfortunately, most laboratory gas chromatograph ovens are incapable of providing heating rates fast enough to take full advantage of the high separation efficiencies afforded by fused silica columns. Alternatively, new heating approaches based on thermal mass minimization have been developed to achieve high column heating rates without dramatically increasing the power consumed by conventional gas chromatograph ovens. The most common method used for achieving faster column temperature ramps utilizes localized heat transfer, which is achieved by positioning the heat source very close to the column [11,12]. This can be accomplished by placing a heating element next to a fused silica column [13], by coating a fused silica column with a metal that is then heated electrically [14], or by using a metal capillary column that is resistively heated [15–18]. In addition to providing high heating rates, locally heated columns can be rapidly cooled by making use of highly efficient fan and baffle cooling systems when they are placed inside commercial instruments. In this manner, “low thermal mass” (LTM) accessories for conventional gas chromatograph ovens can be used to add fast separation capabilities to these instruments.

An alternative approach for achieving fast heating rates involves minimizing the heated “air bath” volume containing the column by reducing the size of the gas chromatograph oven [2]. By reducing the amount of space occupied by the gas chromatography column, it is possible to achieve heating rates approaching those reported for resistively heated columns [19]. Because the oven is typically the largest component in a gas chromatography instrument, the use of a small oven which has been optimized to accommodate a separation column with minimal empty space makes it possible to incorporate fast gas chromatography into analysis systems that occupy

* Tel.: +1 405 325 4811; fax: +1 405 325 6111.
E-mail address: rlwhite@ou.edu

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significantly less space than typical commercial instruments. The apparatus described here, which incorporates a small volume gas chromatography oven, can be used as an accessory to provide fast fused silica column heating for laboratory GC instruments and can also be employed for automated gas stream sampling. Specifically, the automated gas sampling application described here involves successive repeated assays of effluent exiting a thermogravimetry apparatus.

Characterization of volatiles generated during thermal analyses (e.g. thermogravimetry) can provide information helpful for elucidating temperature-dependent reaction mechanisms. The type of analysis needed for evolved gas monitoring depends on the characteristics of the species to be monitored and the rate at which concentrations change. Detection methods that produce a unique, selective response for a specific substance can be employed for monitoring without interference from other species that may also be present in the gas stream. Alternatively, mass spectrometry can provide molecular structure information regarding all volatiles generated during thermal analyses and is commonly employed as an evolved gas analyser [20,21]. Unfortunately, the structural information afforded by mass spectrometric evolved gas analysis often consists of overlapping contributions from multiple mixture components, making species-specific detection difficult or impossible.

The advantages of using gas chromatography for separating volatile mixture components generated during thermal analyses have been known for at least forty-five years [22–24]. Simultaneous qualitative and quantitative analysis of evolved gas mixtures can be attained by combining gas chromatography separations with mass spectrometry detection of mixture components (i.e. GC–MS) [21,25–32]. In fact, several GC–MS evolved gas analysis methods have been developed. The stepwise pyrolysis GC–MS technique involves subjecting a solid sample to sequentially higher temperatures [33–35]. Evolved gases produced while heating the sample to each successively higher temperature are analyzed by GC–MS to yield species-specific concentration versus temperature profiles. Because thermal analysis is paused while evolved gas mixtures are analyzed, chromatographic separations requiring long times and involving multiple GC oven temperature ramps can be employed. Another GC–MS evolved gas analysis technique involves the use of repetitive isothermal separations to analyze gases at equal time intervals while samples are being heated at a constant rate [28–32,36]. By using isothermal gas chromatography separations, GC–MS evolved gas sampling intervals as short as 1–2 min have been reported [28,30,31]. A third approach to GC–MS evolved gas analysis involves the use of fast temperature programmed gas chromatography to separate mixture components. Somewhat longer sampling intervals (3–5 min) have been reported when temperature programmed GC separations are required [29,32]. However, non-isothermal GC–MS must be used when mixture components have significantly different chromatographic retention properties. By sampling at time intervals on the order of a few minutes, fast GC–MS can provide species-specific concentration change profiles for volatiles [37]. When temperature programmed heating ramps are required, cycle times for repetitive GC–MS analyses depend on the length of time required for chromatographic separations and the time required to cool the chromatographic column back to the ramp starting temperature.

2. Experimental

2.1. Apparatus

A custom built mini gas chromatograph oven was combined with a commercial Hewlett Packard (HP) 5890 GC, an HP 5973 quadrupole mass spectrometer, and a DuPont Instruments model 951 thermogravimetric analyzer for experiments described here. The construction and characteristics of the mini gas chromatograph oven have been described previously [19,37–39]. Fused silica columns are heated within a 5 cm diameter × 3.75 cm long aluminum cup. Columns are wound around a stainless steel wire cage that has a 3.75 cm diameter and is 2.5 cm long. Fused silica columns with inner diameters of 0.25 mm or less can be coiled around the cage. The column/cage assembly is inserted into the aluminum cup and fiberglass insulation is added to fill the gap between the column and the inside surface of the oven. Column heating is achieved by hot gas flowing from an aluminum heater tube that is inserted axially into the cup. This tube contains a nichrome wire resistance heater, which heats the ambient air flowing around it. The oven can be heated at a rate of 10 °C/s when 150 W of power are supplied to the nichrome wire heating element. Column cooling can be achieved by using a fan to remove heat from the oven external surface, or by passing chilled gas or liquid nitrogen into the oven.

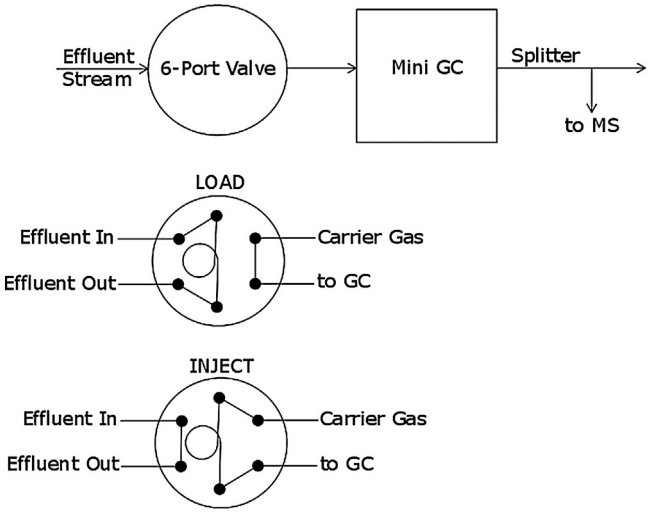

Fig. 1. Schematic of the repetitive injection fast GC analysis mass spectrometer interface.

The mini GC oven was attached to the HP 5890 gas chromatograph for benchmark testing. In this configuration, the mini GC oven was mounted to one of the two injection ports located on top of the HP 5890 GC oven. The ends of a 5 m long, 0.25 mm i.d. DB-5 column with 0.25 μm stationary phase film thickness were threaded through the opening in the top of the HP 5890 GC and connected to the injector and detector fittings inside the HP 5890 oven. The HP 5890 GC injector and FID detector were maintained at 250 °C and the oven was held at 200 °C during chromatogram measurements. Manual 1.0 μL sample injections of a hydrocarbon mixture were made by using a 100:1 split ratio. The column flow rate was adjusted to 1.7 mL/min He. Mixture components were separated by using a temperature program consisting of an isothermal hold at 35 °C for 0.3 min followed by selected heating rate ramps to 250 °C.

The mini GC oven was employed to facilitate repeated analyses of vapor streams containing hydrocarbon mixtures exiting from the DuPont Instruments model 951 thermogravimetric analyzer. A schematic of the automated repetitive injection gas chromatography interface employed for this purpose is shown in Fig. 1. The interface consisted of a heated 6-port sampling valve, the mini GC oven, and a variable splitter valve that connected the end of the mini GC capillary column with the inlet of an HP 5973 quadrupole mass spectrometer. The load and inject 6-port gas sampling valve configurations are shown in Fig. 1. The sample loop volume was 100 μL. The mini gas chromatograph oven was contained within a 20 cm × 15 cm × 7.5 cm aluminum enclosure along with the automated 6-port gas sampling valve (model 6C6UWT, VICI Valco