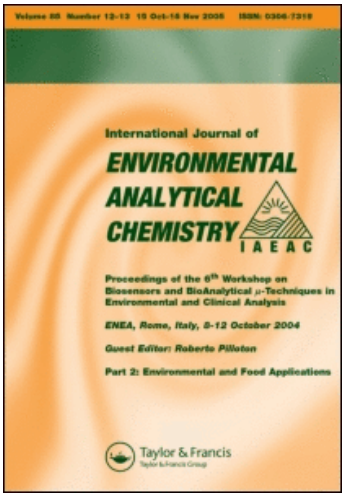

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Measurement of Organic Atmospheric Transformation Products by Gas Chromatography

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MEASUREMENT OF ORGANIC ATMOSPHERIC TRANSFORMATION PRODUCTS BY GAS CHROMATOGRAPHY

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The photooxidation of hydrocarbons in the atmosphere leads to the formation of organic species which are typically more polar in character than the parent compounds. In recent years, detailed hydrocarbon measurements for C_1 to C_{10} alkanes, alkenes, and aromatics in the atmosphere have involved the use of deactivated canisters and gas chromatography, similar to that described by EPA Method TO-14. However, quantitative measurements of atmospheric polar organic compounds by this method are unreliable. Work in this laboratory frequently involves the analysis of sample mixtures from smog chambers that are used to simulate urban atmospheres for studying the formation of ozone and other potentially hazardous compounds. Over the past several years we have developed an inert cryogenic sampling system and related GC methods for the analysis of the photochemical mixtures which are sensitive, reproducible and provide adequate separation for non-polar hydrocarbons and their polar transformation products. These improvements have allowed a number of kinetic and mechanistic studies to be conducted, which in the past have only been possible using in-situ Fourier Transform Infrared Spectroscopy. This paper describes the system development including current strengths and limitations as applicable to experimental programs requiring measurements of polar organic compounds at near-atmospheric concentrations.

KEY WORDS: Gas Chromatography, transformation products, photooxidation, detailed hydrocarbon measurements.

INTRODUCTION

The photooxidation of hydrocarbons in the atmosphere leads to the formation of organic species which are typically more polar in character than the parent compounds. Formation

of these polar compounds facilitates their removal from the air matrix through processes such as wet and dry deposition. However, in urban areas the lifetimes of these airborne compounds and their transformation products can be sufficiently long to allow considerable migration into indoors areas and thus permit human exposure both outdoors and indoors[1]. The potential for some of these products to show genotoxic effects[2,3] suggests the importance of comprehensive programs to identify and measure these compounds in the atmosphere and determine their potential impacts.

Measurement of hydrocarbons in the atmosphere is also important for source-receptor models and for determinations of the formation of ozone in urban areas using urban airshed models[4]. The 1990 Amendments to the Clean Air Act stipulate the use of specific fuels and fuel additives in areas not in compliance with ozone or carbon monoxide standards. Thus, methanol, ethanol, and alkyl ethers (e.g., methyl *tertiary*-butyl ether [MTBE] and ethyl *tertiary*-butyl ether [ETBE]) are being added to automotive fuels at specific periods during the year in many parts of the country. With the increased use of such oxygenated fuels, the pervasiveness of polar compounds such as ethers and alcohols from direct emission sources in urban areas will become important considerations when evaluating VOC loading in urban airsheds. Quantitative measurements of the concentrations for these polar additives will also be required to evaluate the reliability of the source inputs to these models. Methods for monitoring these compounds at atmospheric levels have not been fully designated. In addition, atmospheric measurements of transformation products provide insight into the photooxidation pathways of the parent compounds. This information is important for developing reliable models to predict the impact of these compounds on ozone formation, as well as for predicting concentrations of species other than ozone.

In recent years, detailed hydrocarbon measurements for C_1 to C_{10} alkanes, alkenes, and aromatics have become more sophisticated and have allowed source-receptor models to be developed and evaluated[5,6]. Most successful measurements of hydrocarbons have involved the use of deactivated canisters. This technique has the advantage that hydrocarbon compounds are normally stable and readily recoverable from the Summa polished canisters while capillary gas chromatography (GC) with flame ionization detection (FID) gives good sensitivity with highly resolved peaks. By contrast, quantitative measurements of polar organic compounds with functional groups containing oxygen or nitrogen atoms by this method are somewhat less reliable[7,8]. In special cases, other techniques are used to quantitatively measure polar compounds. For example, measurements of atmospheric levels of reactive carbonyl compounds have frequently involved the use of derivatization techniques which allow preconcentration and high sensitivity[9,10]. Measurements of photooxidation products in the atmosphere by gas chromatography, other than nitrogenated PAHs[11,12], have been relatively sparse.

The major problems associated with the quantitative measurement of vapor phase polar compounds by GC include the difficulty in successful collection and the recovery of these materials for injection into the chromatograph. For sampling at ambient levels, the most common method of collection is the use of a solid phase adsorbent to trap samples from a large volume of air by adsorption followed by recovery of the sample by solvent or supercritical fluid extraction. Sample losses result from incomplete trapping on the adsorbent, incomplete recovery from the adsorbent or decomposition of the sample during the

collection and extraction procedure. A second problem occurs with the difficulty in analyzing these compounds by GC. These chemicals tend to be more easily lost on surfaces and/or more sensitive to decomposition than their parent hydrocarbon compounds. Heated injection ports and active sites in the injection port liners (as well as on internal column surfaces) can cause significant sample loss and poor chromatographic separation and peak tailing. Developments in recent years of cool on-column injection techniques and highly inert capillary columns have helped reduce these problems but do not eliminate them.

The work reported here considers some of these problems related to the analysis of product compounds generated during the irradiation of hydrocarbons in smog chambers. Smog chambers are frequently used to simulate urban atmospheres under controlled conditions to study the formation of ozone and other potentially hazardous compounds[13]. Although these chambers are used to simulate urban settings, they are typically operated using reactant concentrations at a factor of five or more times higher than normal outdoor levels. This approach eases the burden of taking relatively large volume samples from a fixed volume chamber and allows detection of low concentration products while not shifting the relative product distribution. Nonetheless, the analytical methods developed for this system in most cases are directly applicable for samples collected in urban settings.

One consequence of conducting experiments using smog chambers is that ozone concentrations formed under typical reactant conditions are frequently on the order of 500 ppbv. This high ozone concentration restricts the use of solid phase adsorbents such as XAD-2, Tenax or polyurethane foam (PUF) for organic sampling because the adsorbents and in some cases the analytes, react with ozone[14,15] resulting in significant artifact formation and product loss. Consequently, to minimize these problems, the procedures described herein involve the cryogenic collection of the vapor phase products followed by thermoelectric pulse heating and injection onto the GC column for analysis.

Several conditions must be met for the successful preconcentration, injection and analysis of these compounds on a single chromatographic system. First, the trapping efficiency must be essentially complete for all of the volatile species including the C_2 hydrocarbons. This can be achieved at, or near, liquid oxygen temperature with a very low pressure drop across the trap. The system must also be capable of accepting modest levels of water in the sample (e.g., 10,000 ppmv) without plugging the flow through the trap. The heating rate of the trap must be sufficiently fast to inject the compounds in a narrow band but not so great as expose any thermally labile compounds to extreme temperatures before they flushed onto the GC column. The system materials must be highly inert to avoid adsorption or decomposition and reduce tailing of sensitive compounds. Because all of the volatile species are trapped and injected without additional fractionation, the system must be able to chromatographically analyze compounds ranging from extremely non-polar hydrocarbons to polar products such as organic nitrates, ketones, aldehydes and alcohols.

Over the past several years, a chromatographic system has been developed in this laboratory which satisfies most of these requirements with few compromises. In this paper, we describe the development and current state of this system. The utility of the approach is demonstrated by providing examples of its application to current environmental studies.

EXPERIMENTAL

The experimental system used to generate polar organic compounds similar to those produced in urban atmosphere is based around a conventional smog chamber. The block diagram given in Figure 1 depicts the apparatus utilized for generating photochemical mixtures. Reactants are introduced into the smog chamber either by direct injection or by a continuous flow through a mixing manifold. The direct injection approach simulates a static irradiation and allows reactivity and product formation profiles of hydrocarbon mixtures to be collected as a function of time. The continuous flow approach is used to establish a steady state system in which the effluent is used for extensive product analyses, particularly by techniques requiring high volumes of effluent[16]. In either case, effluent from the chamber is drawn continuously through a Teflon sample line at a rate necessary to minimize residence time of the sample. The sample for GC analysis is pulled into the cryogenically cooled trap using a pump and mass flow controller to maintain a constant flow rate. Samples are collected for fixed periods of time and then injected into the GC for analysis. Other associated instrumentation and further details of the chamber operation have been described elsewhere[17].

The sample collection system for GC analysis depicted in Figure 1 is presented in an expanded version in Figure 2. It is largely constructed from commercially available components. It is centered around a heated 10 port rotary valve of Hastelloy 22 (Valco, Inc., Houston, TX) with 1/16″ fittings having a 0.030″ bore, a valve heater (Valco, Inc.) and the

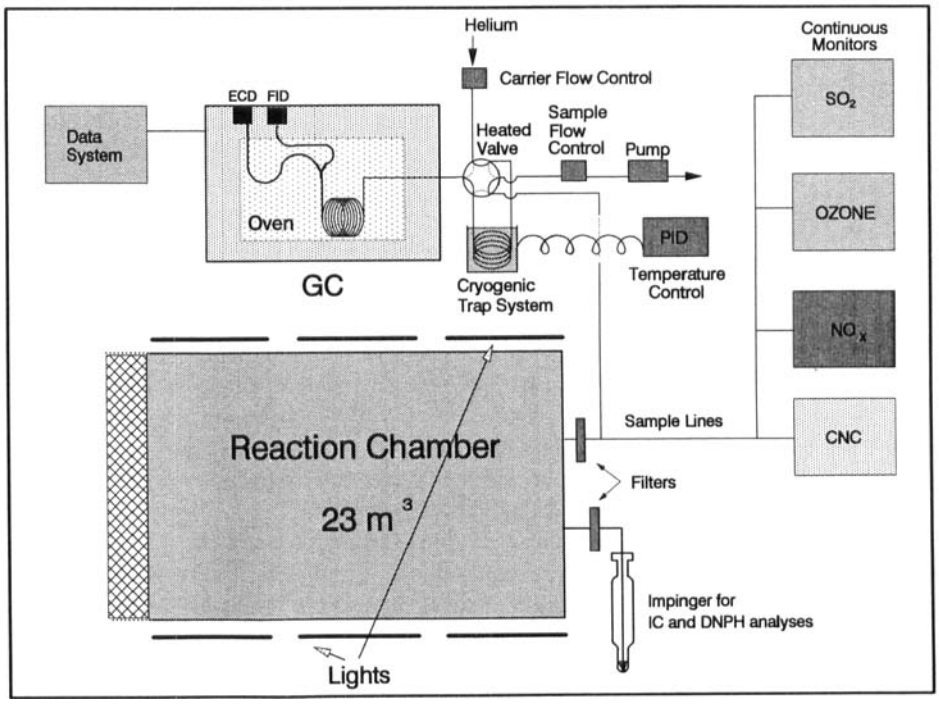

Figure 1 Schematic of experimental system to generate photochemical oxidation products.

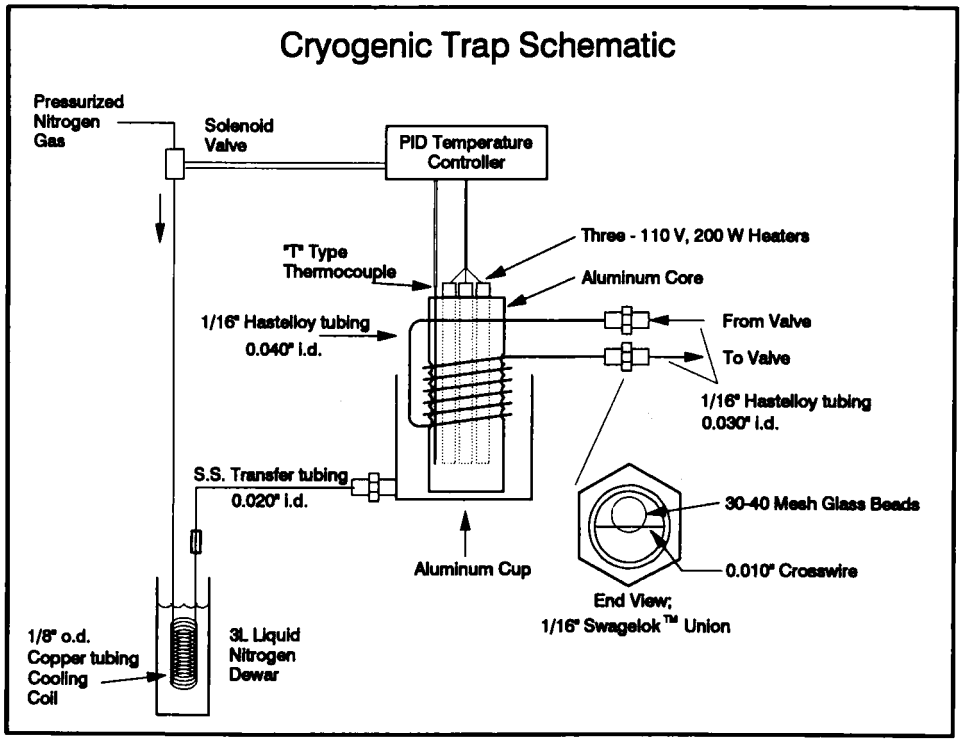

Figure 2 Expanded view of collection system for air samples.

sample trap itself. The packed portion of the trap is constructed from 1/16″ × .040″ i.d. Hastelloy C tubing (Corrosion Materials, Inc., Baker, LA) while the transfer line between the trap and valve is 1/16″ × 0.030″ Hastelloy C tubing (Valco, Inc.). Although a six port valve configuration could have been used to operate the system, the 10 port valve allows other configurations not described here. The trap tubing is tightly wound around a machined aluminum heating core. To retain the glass bead packing in the tubing, a stainless steel wire (0.010″ diameter × 1/16″ long) is placed across the inner lip of each 1/16″ Swagelok™ union with the 1/16″ tubing butted against the wire. With the ferrule and nut tightened, the tube seats against the wire creating a tight seal for the glass beads to lodge against during packing. Prior to final assembly, all of the inside surfaces of the inlet tubing, trap tubing, fittings and retaining wire are custom coated and deactivated by the Restek Silcosteel™ process (Restek, Inc., Bellefonte, PA). The treatment is applied after the tubing has been bent around the heating core and fitted with the cross wire but before being packed with glass beads. Following the Silcosteel™ treatment, clean, acid-washed glass beads having a 30-40 mesh size (Potters Industries, Inc., Brownwood, TX) are drawn into the trap using a vacuum pump. The bead diameter is sufficiently large so that the beads are retained in the trap tubing by the internal crosswire. The beads and inner surfaces are then silanized with dichlorodimethyl silane and baked out under helium at 300 °C for several hours. This comprehensive process

reduces the heated metal contact of organic constituents to only that of the highly inert Hastelloy 22 valve.

Heating and cooling of the sample trap is controlled by an Omega 2012 "Ramp and Soak" process controller (Omega Engineering, Inc., Stamford, CT) outfitted with a "T" type thermocouple for monitoring temperature. The trap can be heated or cooled on command over the entire temperature range from −195 to 300°C. Three 200 watt resistance heaters (3/16″ × 1 1/2″, Omega Engineering, Inc.) are inserted inside the aluminum core to permit rapid heating of the trap. The entire assembly is then mounted inside an insulated aluminum cup which confines and focuses the coolant flow. Pressurized N_2 gas is used to cool the trap by condensing the gas in an 1/8″ coiled tube immersed in a dewar of liquid N_2. A solenoid valve modulates the injection of the condensed nitrogen into the cooling cup. This procedure allows addition of the cryogen to be finely controlled.

Operation of the gas chromatography system was also comprehensively evaluated. Gas chromatographs using constant pressure carrier gas control can have carrier flows that vary over the programmed temperature range due to changes in gas viscosity with temperature. Column temperature requirements to resolve the C_2 - C_{10} organic compounds range from −50 to 200 °C. Cryogenically cooled oven temperatures are used at the start of the chromatographic runs to maintain sharply focused peaks of the low boiling compounds. Column temperature is then incrementally increased to effect elution and resolution of the intermediate and higher boiling point compounds. Such drastic changes in column temperature significantly affect the viscosity of the carrier gas resulting in dramatic changes in carrier gas flowrate and ultimately in the column separation characteristics. In order to maintain optimum carrier flow velocity throughout the temperature program, a constant velocity carrier gas system is used. Initially for the HP 5890A GC, the constant carrier gas flow was maintained with an external mass flow controller (FC260, 10 SCCM; Tylan, Inc., Torrance, CA). With a suitable pressure differential, the controller maintained a constant carrier flow regardless of the oven temperature program. Recently, we have used the programmable carrier gas flow option available on the HP 5890 Series II GC. A 1/8″ Swagelok™ tee can be placed in the carrier gas split vent return line from the injection port. A line can then be directed to the rotary valve carrier gas port from the tee. Then, by plugging the column outlet on the injection port, the carrier gas flow on the trap and the rotary valve inject port can be programmed directly from the front panel on the GC. The heating rate on the trap is sufficiently fast that carrier flows in the range of 1/2 - 2 ml/min allow most of the analytes to be injected onto the column in a narrow band suitable for high resolution capillary chromatography without using a second cryofocusing unit as in some commercial purge and trap instruments. Cryogenically-cooled oven temperatures are then only required in this system at the start of the chromatographic runs to achieve focused peaks for the lowest boiling compounds (C_2 and C_3 paraffins). For analyses where these are not of interest, oven temperature programs can begin at ambient levels or higher.

The trap is cooled to −181 °C (the boiling point of oxygen) to prevent the collection of liquified gases, such as oxygen or argon in the loop. Known air volumes are collected by drawing sample through the inlet system at a constant rate for a fixed period of time using a pump and a 0–100 cm^3/min mass flow controller (Tylan, Inc.). A 1/8-in. stainless-steel, three-way valve located on the sample inlet line outside of the heated box is used to flush

the loop with carrier gas prior to injection. Without the purge, high concentration analytes present in the short, uncooled section of the sample loop will appear as ghost peaks from an unavoidable injection as the valve position is switched. After collection, samples are injected onto the GC column by flash heating the loop with the thermoelectric heater to 260 °C. At full power, the heating rate of the trap assembly is approximately 12°C/sec. This rapid but controlled heating of the loop minimizes losses of compounds that are thermally sensitive while providing a high quality injection of most analytes.

Analyses of the organic components are performed using a variety of instruments and configurations. Routine quantitative analysis of most analytes is performed by using a Hewlett-Packard (HP) 5890 Series II GC equipped with an FID and an ECD, an HP3396B dual channel integrator, and a MS-DOS data acquisition system with Chrom Perfect™ (Justice Innovations; Palo Alto, CA) chromatographic software. Compounds are separated by one of the following column configurations: (1) Hewlett-Packard HP-5 capillary column (0.32-mm i.d., 50-m length, 1-μm film thickness), (2) a Hewlett-Packard HP-5 megabore column (0.53-mm i.d., 25-m length, 2.65-μm film thickness) or (3) a J&W DB-1 capillary column (0.32-mm i.d., 60-m length, 1-μm film thickness) directly coupled to a Restek Stabilwax™ column (0.32-mm i.d., 30-m length, 0.5-μm film thickness) using a Restek fused silica Universal Press-Tight™ capillary column connector. A 0.53 mm i.d. deactivated fused silica retention gap is directly connected to the heated valve with a special nut and ferrule (Valco, Inc.) and to the analytical column also using a Press-Tight connector. Depending on the application, hydrogen or helium is used as the carrier gas and maintained at constant velocity using one of the previously mentioned configurations. The GC oven temperature is programmed according to the boiling points of the analytes detected.

Effluent from the GC column is split approximately 8:1 between the FID and ECD detectors by using a deactivated fused silica Y-splitter and unequal lengths of deactivated, uncoated fused silica tubing. As a result both detectors respond to the same chromatographic peaks, thus providing additional information for the identification of unknown products. For example, products containing strong electron-capturing functional groups such as organic nitrates will be readily detected by both detectors, whereas compounds such as aldehydes would be only weakly detected by the ECD while hydrocarbons have no response on the ECD. This information combined with the GC-MS data helps significantly in the identification of unknown compounds.

Product identifications are performed with the use of an HP 5985A GC-MS system retrofitted with a Vector One data acquisition and analysis system (Technivent, Inc.; St. Louis, MO). GC sampling and separations with this instrument are performed using the same column and inlet configuration as on the GC-FID/ECD system to duplicate the chromatographic conditions as closely as possible. The instrument has been retrofitted with a direct capillary inlet (Scientific Instrument Services, Inc.; Ringoes, NJ) for the MS. However, instead of inserting the analytical column into the MS source directly, a short piece of deactivated fused silica capillary column (1m × 0.4 mm o.d. × 0.1 mm i.d.) is inserted into the source with the analytical column directly attached to this tubing using a butt joint connector (Supelco, Inc.; Bellefonte, PA). The MS pumping system is only able to draw 0.5-1.0 mL/min of He across the pressure drop created by the narrow bore capillary at atmospheric pressure. Thus, at typical pressures required to operate wide bore (0.032 mm

i.d.) capillary columns, flows of 1-2 mls/min can easily be achieved. The resulting configuration creates a pressure driven system across the analytical column allowing the use of the wide bore columns at optimum chromatographic flow rates. Moreover, columns can be changed quickly without venting the mass spectrometer.

Sample collections on the cryogenic loop (for all chromatographic systems) are taken for 2-10 min at 10-75 mL/min and then flash injected into the GC. Multipoint calibration curves over ranges appropriate to the individual components are used for quantitative measurements of known compounds. Prior to incorporation into standard solutions, each standard component is evaluated for purity and for potential wall loss in the vapor phase. Standard solutions are made from dilutions of the various components typically into methanol. Vapor phase calibration standards for quantitative GC-FID measurements are then generated each day by injecting known liquid volumes of the standard solutions into measured volumes of ultrazero air in Teflon bags. This approach facilitates the injection of a sufficiently large volume of liquid to produce suitable reproducibility for the day-to-day calibrations. The calibration factors are generally calculated from peak areas. Standards are run each day at the beginning and end of each set of experiments to determine calibration factors and check the instrumental performance.

Sampling volume, collection efficiency and FID response are regularly checked using an undiluted, NIST propane standard, having nominal concentration of 3 ppmv in air. This is performed by filling an evacuated Teflon bag with the standard mixture and then drawing known volumes of sample at different flow rates through the trap and comparing FID response. Reproducibility for replicate standard samples collected for the same collection time and flow rate typically have a relative standard deviation (RSD) of approximately ±1.0% (3 samples on the same day) while samples with equal volume but collected at different flow rates and sample times have an RSD of about ±2.0%. Large deviations of >5% on a day-to-day basis usually indicate either a leak, detector problems, sample breakthrough or problems with the flow controller calibration. The current configuration of this system has evolved through several stages of development. The following section will discuss these developments in terms of choice of materials and chromatographic performance.

RESULTS AND DISCUSSION

Much of our earlier work was performed using an open tubular, fixed volume loop and packed column GC. In an effort to improve the sensitivity and separation of hydrocarbons and polar compounds, an unsopisticated system using a 1/6" o.d. open tubular trap interfaced to a capillary column GC through a rotary valve was constructed. The system used liquid argon or oxygen to cool the trap during sample collection and boiling water for flash heating and injecting the samples into the GC.

A number of problems were encountered including breakthrough of the light (C_2 - C_3) hydrocarbons at relatively low collection rates (>5 mL/min) and peak splitting of some of the low boiling components. The trap was packed with deactivated glass beads (60–80 mesh) from a chromatographic supplier to prevent the breakthrough problem. The beads were retained in the tube by packing 1/16" Swagelok union fittings with silanized glass wool.

This approach solved the breakthrough problem and reduced the peak splitting, but the large pressure drop across the packed trap reduced the flow through the loop to less than 10 mL/min on the pull-through system. Also, if water was present at even relatively low levels (1-5% RH) in the flow stream, it would quickly cause blockage of the tightly packed loop and prevent further sample collection. Because sample sizes of 250–500 mL are frequently necessary to investigate the low concentration products from these photochemical systems, sample collection times of 30–60 minutes became prohibitive.

This problem was alleviated by repacking the trap with much larger glass beads to reduce the pressure drop during sampling. By using 1/16" o.d. tubing with 0.040" i.d. for the trap, 30–40 mesh (425 to 600 μm diameter) glass bead packing will, on the average, have a diameter slightly larger than one half the inner diameter of the tubing. This packing yielded much larger interstitial spaces while still providing a large surface area and a tortured path for efficient trapping during sample collection. The pressure drop across the trap was reduced substantially allowing collection rates of up to 75 mL/min.

This collection system worked satisfactorily for a preliminary studies involving auto exhaust emissions, however, during a study of the photooxidation of methyl *tertiary*-butyl ether (MTBE), other problems were encountered. First, there was more peak tailing in the chromatograms of MTBE and its major oxidation product, t-butyl formate, than had been previously observed from the hydrocarbon peaks from auto exhaust. A sample chromatogram illustrating this problem is shown in Figure 3a. A number of steps were taken to alleviate this problem. The valve was wrapped in heating tape and operated at 100°C. While this change resolved the tailing problem, the t-butyl formate began to decompose on the heated stainless steel valve surface. It appeared that nitrous acid (HONO) (which had been added as an OH radical source in the photochemical mixture) had caused activation of the stainless steel surface. At the recommendation of technicians at Valco, Inc., a new valve comprised of Hastelloy™ 22 was obtained. (Hastelloy is a special, highly inert stainless steel alloy.) In addition, 1/16″ × 0.030″ i.d. tubing of Hastelloy C was used to replace most of the transfer lines while the trap itself remained 1/16″ × 0.040″ i.d. 316 stainless steel. A source for 1/16″ × 0.040″ i.d. Hastelloy C tubing could not be located at that time, but it was felt that the majority of the sample would be collected on the deactivated glass beads and would not be exposed to the stainless-steel surface. As seen in Figure 3b, this expectation is borne out by the excellent chromatography for *t*-butyl formate following these adaptations. (Note that while the column is the same, the conditions are not identical resulting in different retention times.)

Most of the products in the photooxidation systems are somewhat polar with oxygen or nitrogen containing functional groups. Many may have more than one functional group and many have boiling points substantially higher than 100 °C. The use of boiling water and a valve heated to 100 °C posed the potential for the poor recovery of these compounds. In order to improve on the existing system, a thermoelectric heating system with a higher injection temperature was needed to reduce the loss of products with low vapor pressures. Therefore, we adapted a system, previously described for analyzing Tenax cartridges[18], to improve the recovery and analysis of these compounds. This has led to the system described above. These changes have led to several significant improvements in the resulting system over previous methods.

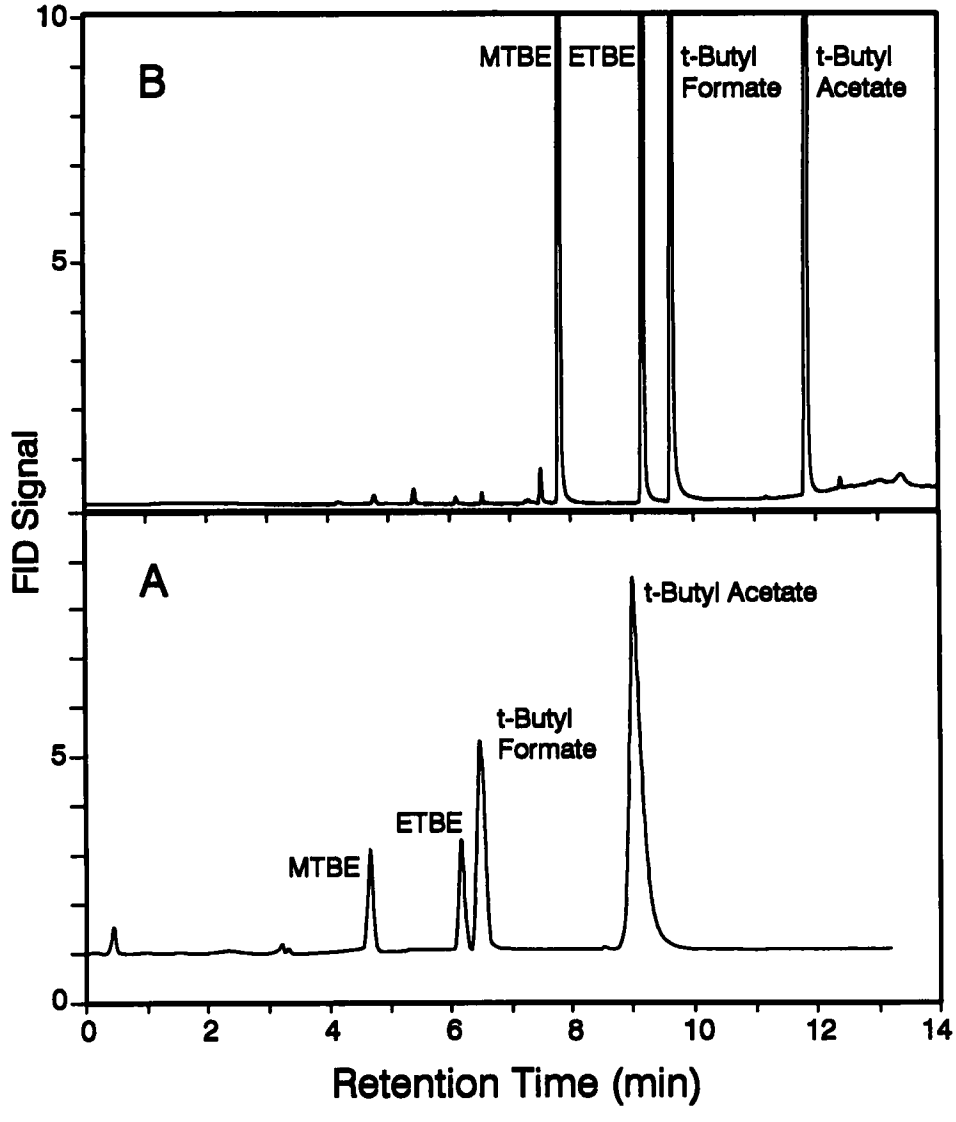

Figure 3 (a) Chromatogram of methyl *t*-butyl ether (MTBE), ethyl *t*-butyl ether (ETBE), and their oxidation products before improvements in valve and associated hardware; (b) chromatogram of same species following improvements.

First, the thermoelectrically heated trap can be readily heated to 300 °C, a temperature substantially higher than obtained with boiling water. While the heating rate to 100 °C is slower than the near instantaneous rate achieved when using boiling water, the heating system provides for an extended range. This moderately broadens the peak widths of very low boiling compounds such as the C_2 and C_3 hydrocarbons. On the other hand, the average

heating rate of 12 °C/sec may help recover thermally-labile compounds by allowing them to flush from the trap without experiencing extreme heat. Moreover, the Omega programmable integral/derivative (PID) temperature controller offers the possibility of using slower controlled heating rates or even including plateaus in the heating ramp, although these possibilities have not been employed. The PID controller also offers significant flexibility for controlling the collection temperature of the cold trap. The PID is capable of maintaining trap temperatures down to −195 °C using pressurized liquid N_2 modulated by a solenoid valve and easily maintains liquid oxygen temperature (−181 °C) to avoid collection of the condensable gases oxygen and argon.

Second, the addition of the crosswire in the Swagelok union to retain the glass beads in the trap reduces the pressure drop across the trap as compared to the glass wool plugs used in the earlier designs. This also helps prevent the permanent collection of non-volatile particulate matter (formed during some photochemical reactions) which eventually blocks the glass wool plugs or produces ghost peaks from partially adsorbed or decomposed analytes. Furthermore, the trap can be cleaned without disassembly simply by removing it from the rotary valve and flushing it with solvent.

Finally, the treatment of the inner surface of the tubing using the Silcosteel process provides essentially complete protection of the analytes from heated metal surfaces in the trap and transfer lines. Although we have not noticed any difference in the performance of the uncoated Hastelloy traps compared to the Silcosteel traps, the treatment provides added insurance against decomposition. Furthermore, it allows the *in situ* silanization of the glass beads in the packed traps. Thus, this configuration leaves the Hastelloy 22 valve as the only heated metal surface which comes into contact with the sample.

Table I shows the collection efficiency of several light hydrocarbons at four flow rates. The collection efficiency of the trapping system is essentially 100% for the C_2 and higher hydrocarbon compounds at a collection rates of ≤ 25mL/min and trap temperatures of − 180 °C. Sample collection flowrates above 25 ml/min were tested with some loss of ethane. At 75 ml/min complete loss of ethane and partial loss of ethylene was observed. Moreover, the chromatography can be adversely affected for the lower boiling compounds at high collection rates, because they tend to be trapped in a broader band than higher boiling compounds which degrades the quality of the injection even if the heating is instantaneous. Thus for accurate, reproducible analyses of the C_2 compounds, sample collection rates are limited to 25 mL/min.

Table 1 Trap Collection Efficiency (%)

	Collection Flow Rate (mL/min)			
Compound	*25*	*40*	*50*	*75*
Methane	—	—	—	—
Ethane	100	80+	—	—
Ethylene	100	100	100	80+
Propane	100	100	100	100
Propylene	100	100	100	100
Isobutane	100	100	100	100

Notes:
(1) RSD for replicate samples = ±1%
(2) RSD for equal volume samples at different flow rates = ±2%

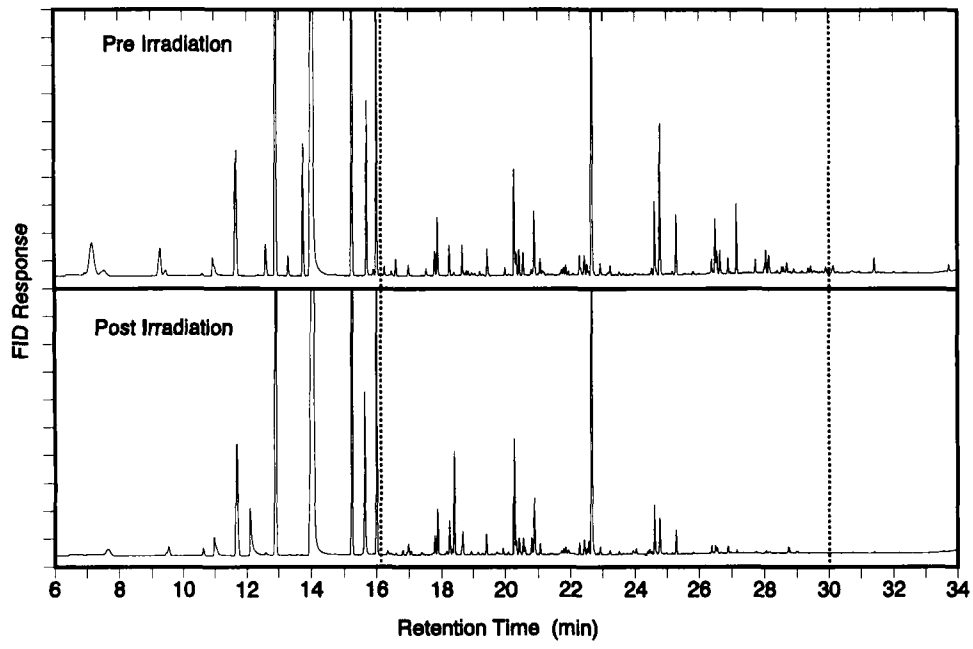

Figure 4 Chromatogram of detailed hydrocarbons from methanol exhaust. Methanol elutes at 14.1 min and is separated from the C_4 hydrocarbons. Most of the smaller peaks while not named have been identified.

Figure 4 shows chromatograms from an irradiation of auto exhaust of an alternative-fueled vehicle operated with M85 (85% methanol, 15% gasoline). Although the fuel composition is 85% (v/v) methanol, approximately 60% of the non-methane exhaust products are hydrocarbons. From the sharp peak shapes it is evident that the injection system efficiently traps analytes and injects the compounds in a narrow band allowing good chromatographic separation. The top chromatogram represents the pre-irradiation mixture. At retention times of 7–7.5 min, ethylene and ethane are satisfactorily separated while at 8.5–8.7 min propylene and propane are baseline separated. As mentioned, the peaks for these very low boiling compounds are marginally broader than the other components in the mixture.

In addition, methanol is separated from the C_4 and C_5 hydrocarbons as seen by the sizable peak at 14.2 min. In a typical analysis of this fuel system using a 60 or 90 m SE-30 (or equivalent) stationary phase column, the methanol peak is badly shaped and co-elutes with *n*-butane. To effect the separation shown in Figure 4, the 30-m Restek Stabilwax column is coupled sequentially following a 60m DB-1. This column combination helps improve the methanol peak shape and shifts the peak retention time to a position between the C_4 and C_5 hydrocarbons. Although there is the potential for some band broadening of the hydrocarbons with the additional length of column, in practice, the addition of the carbowax column shows a negligible effect on the peak widths of the normal hydrocarbons.

From the irradiated mixture shown in the bottom chromatogram of Figure 4, three photooxidation products can be readily detected—acetaldehyde at 12.1 min, acetone at 15.6 min, and methyl ethyl ketone at 18.3 min. The acetaldehyde peak is somewhat tailed but

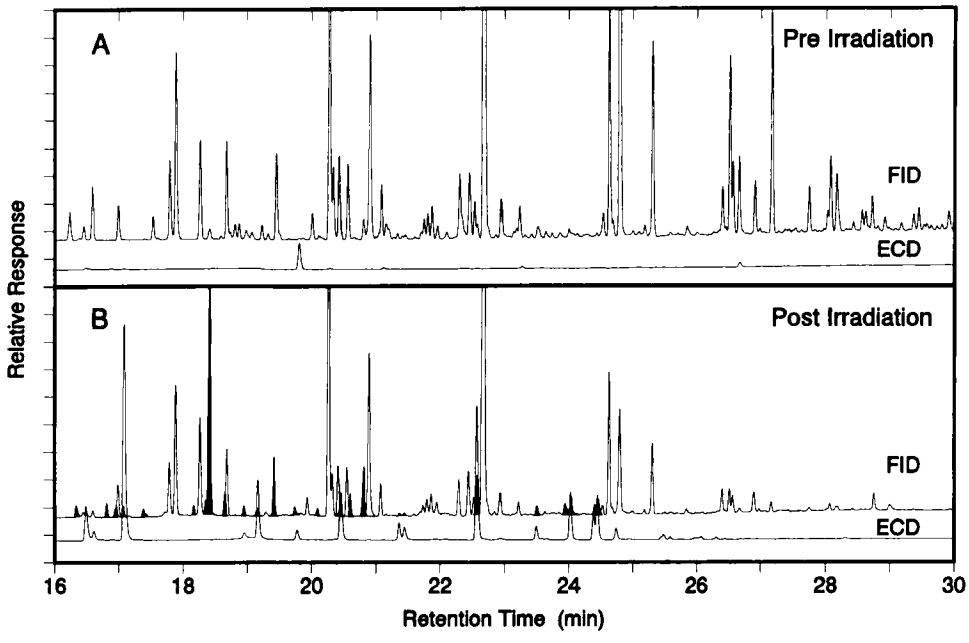

Figure 5 (a) Expanded view of chromatogram in Figure 4 before irradiation. (b) Same chromatographic region showing loss of reactants and formation of products following irradiation of the exhaust mixture as determined by simultaneous FID and ECD detection.

acceptable while the other components are well resolved with excellent peak shape. Figure 5 shows an expanded section of this chromatogram from 16 to 30 minutes with the simultaneous ECD and FID detector traces. A close examination shows significant differences in the pre- and post-irradiation mixtures. As many as twenty different product peaks can be seen in the post irradiation mixture (shaded peaks) all of which most likely contain polar functional groups. The overlying ECD peaks suggests those containing nitro or nitrate groups. This determination may be important because these types of compounds may contribute significantly to the observed genetic activity of photochemical mixtures[19]. At present only two of these products have been identified; methyl nitrate at 17.1 minutes and a branched C_5 nitrate (probably 2-methyl-2-nitratobutane) at 22.3 minutes. Work is proceeding to identify these other product compounds.

This column combination has also worked well in solving other separation problems which we have experienced. For example, in a study of the kinetics and photooxidation products of ethyl *t*-butyl ether (ETBE)[20], separating all of the products on a single chromatographic column was extremely difficult. In two cases, the products were similar in polarity and boiling point to either the parent compound or to another product. In one case, ethyl acetate and t-butyl formate were difficult to separate from the parent ETBE, which was present in relatively high concentration. A second problem was the separation of a potential product (*t*-butyl alcohol) from other compounds present in the system (e.g., methyl nitrate and t-butyl nitrite). However, Figure 6 depicts a GC/MS total ion chromatogram of the

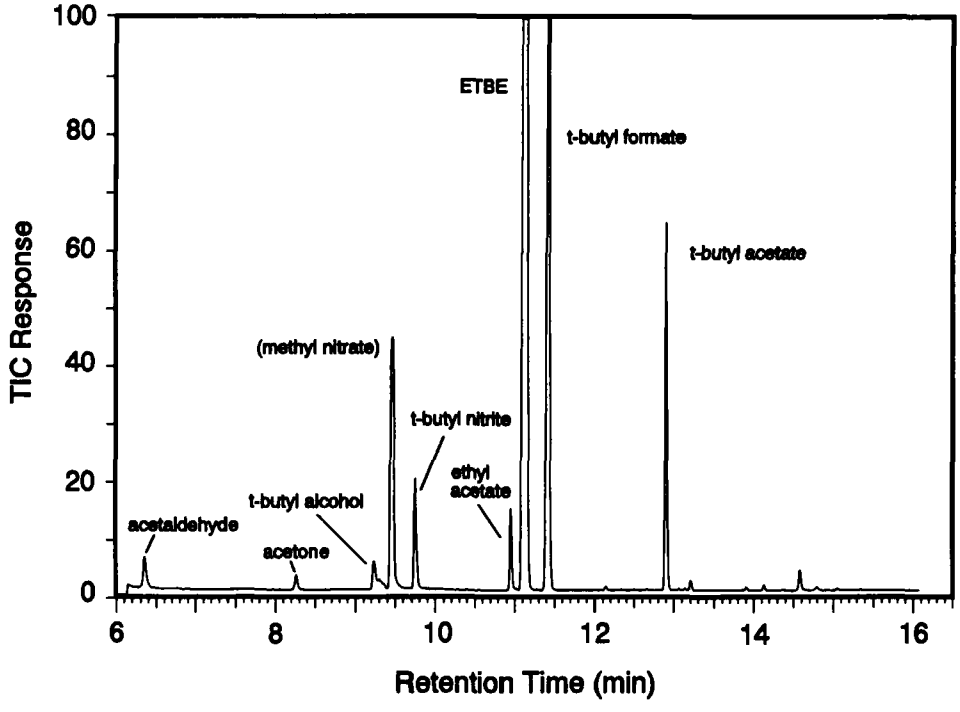

Figure 6 Separation of products following irradiation of ETBE. With ETBE at high reactant concentrations, ethyl acetate and *t*-butyl formate will coelute with ETBE under former chromatographic configuration.

successful separation of all of the photooxidation products of ETBE using the two column technique combined with the inlet system. Using GC-FID, quantitative yields for each of the products were determined resulting in a carbon balance of 98% from this photooxidation system with the 95% confidence interval not exceeding 8% for any one compound. Only the high quality of the separations and the reproducibility of the trapping system could allow this level of performance.

Another example of the utility of this system comes from examining primary products from the oxidation of toluene. The three chromatograms in Figure 7 are from a product study of irradiations of toluene with methyl nitrite (as an OH radical source) and nitric oxide. In this study the 50-m HP-5 column was used with H_2 as the carrier gas. The column was programmed from 0 °C to 210 °C at 10 °C/min. The top chromatogram is the pre-irradiation sample, which shows methyl nitrite eluting at 2.2 min, toluene at 9 min, and a number of trace contaminants in toluene representing 0.02% total carbon. The bottom two chromatograms are the simultaneous ECD and FID traces after a short irradiation period in which 6% of the toluene is removed. A number of polar products can be identified- 1) benzaldehyde, 2) o-cresol, 3) m,p-cresol, 4) o-nitrotoluene, 5) benzyl nitrate (tentative), 6) m-nitrotoluene, 7) p-nitrotoluene, 8–10) nitrocresol isomers. The peak shapes for these compounds are very good, even for the cresols and nitrocresols, which are frequently

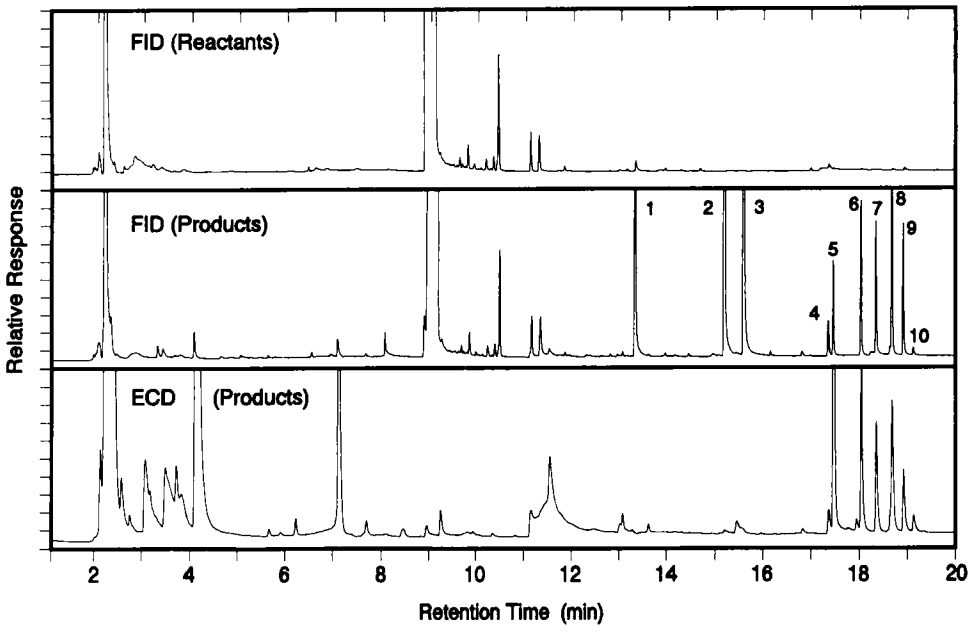

Figure 7 (a) Initial toluene/CH_3 ONO/NO mixture before irradiation (FID). (b) Post irradiation with a total loss of 5% of the toluene. (c) Simultaneous ECD plot from the same experiment.

difficult to analyze. These observations suggest that the surfaces of the apparatus are highly inert throughout and that the heating rates are satisfactory. Moreover, the product peak areas are highly reproducible for replicate experiments, suggesting that recovery from the trap is essentially complete.

This system does have some limitations, however. The product compounds shown in Figure 7 represent no more than 40–45% of the total loss of toluene. (The poor carbon balance represents one of the major limitations in studying mechanisms of the photooxidation of aromatic compounds.) The photooxidation of toluene proceeds by both ring-retaining and ring-fragmentation mechanisms. While one of the ring fragmentation products (4-oxopentanal) co-elutes with an m,p-xylene contaminant at 10.7 min, none of the other fragmentation products are readily identifiable. It is not known whether their concentrations or FID sensitivity are so low that they are not detectable or if they are lost to the reactor walls. Another product, which has been previously reported[21], methyl benzoquinone, is also not found in this chromatogram. We have found that changing the carrier gas from hydrogen to helium resolves the problem. Under these conditions, the compound elutes between benzaldehyde and o-cresol. It is not known if the H_2 reacts directly with the methyl benzoquinone or if metal or other surface is activated to catalyze the decomposition or polymerization of this product. While there does not seem to be any change with the other peaks in the chromatogram, the problem is being investigated further to determine if other compounds act similarly in other systems.

Another limitation results from the difficulty in measuring peroxyacetyl nitrate (PAN) and related peroxyacyl nitrates produced in this type system. PAN is thermally labile with a decomposition half life of 45 minutes at 25 °C and 300 msec at 100 °C. In our system it probably decomposes in the trap or on the column before it can be measured under normal operating conditions. However, we have found that it can be cryogenically collected through a room temperature valve system, flashed off at a slower heating rate and successfully measured by capillary GC if the oven program is set to allow for the peak to elute before the oven temperature reaches approximately 30 °C. Low detector temperatures are also necessary to obtain the full response of this compound. Because of these problems and the importance of the compound, we normally employ a dedicated system for the measurements of these compounds.

Finally, there have frequently been substantial problems with the trap blockage with excess water when the sample collection size exceeds approximately 400 mL and when the absolute humidity is significantly greater than 0.5% (v/v). We have experimented with 1/8″ tubing traps and 14–18 mesh beads to reduce water blockage. This system successfully collects large samples (400–500 mL) at absolute humidities as high as 2%. This represents 5–6 μl of H_2O, however, and is beyond the tolerance limits for both the detectors and chromatographic system. The larger trap is also somewhat more difficult to heat in a manner which allows focussing of lower boiling compounds in a narrow band on the column. However, efforts continue to successfully resolve these problems.

There are several potential improvements in the development of the inlet for future use. One is to expand the use of 1/8″ o.d. tube traps. This allows increased sample loading and with minimum blockage from water. Another possible improvement is to use programmable flow control of the carrier gas. By slowing the flow for the initial heating ramp, band spreading could be reduced for the extremely volatile compounds and the overall chromatography could be improved.

CONCLUSIONS

This project was initiated to improve on the sensitivity and separation quality of analyses of atmospheric hydrocarbons with particular application for use in a smog chamber. However, the apparatus has evolved into a system capable of measuring a wide range of atmospheric polar and non-polar compounds at the part-per-billion level.

The system incorporates several concepts aimed at reducing problems often associated with the use of cooled metal traps. The use of relatively large glass beads (30–40 mesh) with a restraining cross wire for maintaining the packing has several advantages. First, blockage by water, particulate matter or other non-volatile species is significantly reduced, which in turn reduces the potential for chromatographic ghost peaks. Moreover, the back pressure across the system is greatly reduced allowing quantitative sample collection at flow rates up to 75 mL/min even for low boiling compounds such as propane with a sampling reproducibility for the same sample of ±1.0%. In addition, the Silcosteel coating in the tubing allows *in situ* deactivation of the beads with dichlorodimethylsilane insuring a deactivated surface throughout the system. The sample experiences limited metal contact and then only with the

highly inert Hastelloy 22 rotary valve. The efficacy of this system has been shown through several examples of complex photochemical systems.

Disclaimer

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