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INSTRUMENTATION FOR AUTOMATED THERMAL DESORPTION–PYROLYSIS CAPILLARY GAS CHROMATOGRAPHY

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SUMMARY

Instrumentation is described to perform automated thermal desorption–pyrolysis capillary gas chromatography. The evolved compounds are cryogenically trapped to minimize peak width and to isolate the chromatographic column from reactive atmospheres, if necessary. The instrument is operated in the splitless mode to maximize sensitivity.

^{14}C organic compounds were used to determine the transfer efficiencies of polar compounds through the instrument. The absolute recovery of pyrolysis products from the decomposition of [^{14}C]polystyrene was determined. Losses of pyrolysis products to the pyrolysis unit and interface are discussed.

INTRODUCTION

Thermally based sampling techniques encompass a range of experiments that includes both thermal desorption and pyrolysis–gas chromatography (Py–GC). There are three general events that can occur during the sampling process. Mild temperatures (*ca.* 250°C and below) cause the release or thermal desorption of adsorbed volatile compounds from a substrate. No new compounds are formed. Pyrolysis occurs when a sample is heated to higher temperatures, typically 300°C or higher. Py–GC is the subject of several review articles[1–3]. If a reactive atmosphere is used, a third reaction can take place. New compounds can be formed by reaction between the sample and the atmosphere.

Py–GC is used for the identification, quantitation, and characterization of many materials, including synthetic and natural polymers, foods and fossil fuels. Mechanisms are often proposed to explain the thermal degradation pathways of the compounds. Unfortunately, the absolute mass recovery of the material being studied through the pyrolysis, transfer, and separation processes is not determined. Therefore, it is possible that proposed mechanisms could account for only a small fraction of the entire thermal degradation process. More importantly, compounds lost to the "system" may generate a distorted pyrolysis or thermal profile. This will result in a misidentification or poor quantitation of an analyte. Radiolabelled compounds were used by Rodriguez *et al.*[4], to determine absolute recoveries of compounds passed

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through fused-silica capillary chromatographic columns. We have extended the use of radiolabelled compounds to thermal and pyrolysis studies to determine the absolute transfer efficiency of compounds through our system, to determine the percentage of compound pyrolyzed or thermally evolved, and to make apparent the analyte peaks present in a complex chromatogram containing matrix peaks.

In this article we describe the automated instrumentation developed to perform the thermal desorption and Py–GC experiments. Compounds evolved during the sampling process are transferred to the capillary column in a non-splitting mode to make analyses possible at trace levels. The automated cryogenic traps maximize chromatographic resolution, concentrate evolved compounds, allow both long sampling times or slow sample heating rates, and provide for using non-inert atmospheres incompatible with chromatographic columns. The system is designed to minimize active surfaces so that polar compounds can be transferred, separated, and detected. The programmed-temperature quartz sampling interface is used to minimize or eliminate premature thermal degradation of the sample. Radiolabelled compounds are used to determine absolute recoveries of compounds through this instrument and to study the pyrolysis process.

EXPERIMENTAL

Instrument design

The pyrolysis interface, liquid-nitrogen-cooled cryogenic traps, electronic temperature controllers, and valve oven for the thermal sampling instrument (TSI) were constructed with readily available parts. The necessary components and equipment are summarized in Table I.

Programmed initial-final temperature pyrolysis interface. A schematic diagram of the thermal sampling interface is shown in Fig. 1. The quartz tube (7 mm I.D. × 9 mm O.D., Quartz Scientific, Fairport Harbor, OH, U.S.A.) was wrapped with glass tape (Scotch No. 69, 3M, St. Paul, MN, U.S.A.), and then wrapped with 26 gauge glass insulated nichrome wire (Berquist, Minneapolis, MN, U.S.A.) for heating. A J-thermocouple was placed onto the interface and a second layer of glass tape added for electrical insulation. Stainless-steel tubing (1/16 in. (0.16 cm) O.D. × 0.02 in. (0.5 mm) I.D.) was brazed into a hole in the side of a 3/8 in. (0.95 cm) × 1/4 in. (0.64 cm) reducing union (Swagelok) to provide the sampling atmosphere gas flow. The union was drilled through to 9/32 in. (0.714 mm) diameter so the pyroprobe would fit inside it. A 1/8 in. (0.32 cm) × 1/16 in. (0.16 cm) reducing union was partially drilled out to reduce its internal dead volume. This fitting connected the 1/8- in. (0.32-cm) quartz tube of the interface to the first high-temperature valve using uncoated fused-silica capillary tubing (0.21 mm I.D., Hewlett-Packard) as the transfer line. The quartz pyrolysis interface was mounted on the exterior of the gas chromatograph directly over the valve oven. The transfer line between the interface and the valve oven is heated.

Modification to valve oven of gas chromatograph. The gas flow between the quartz interface, valve oven, cryogenic traps, and chromatographic column is shown in Fig. 2. The two high-temperature, zero-dead-volume valves are mounted inside the valve oven on the right-hand side heater block. The built-in actuators of the gas chromatograph are used to switch the valves. A section of the left-hand side heater

TABLE I

APPARATUS

Component	*Model number*	*Manufacturer*	*Conditions/requirements*
Gas chromatograph	5880	Hewlett-Packard, San Diego, CA, U.S.A.	Flame ionization detector–nitrogen photometric detector–flame photometric detector valve oven capillary Level IV cassette analog output cryogenic oven
High-temperature GC valves (2)	9103 HT	Valco, Houston, TX, U.S.A.	Hastalloy-C 4-port
Pyroprobe	122	Chemical Data Systems, Oxford, PA, U.S.A.	Extended time/temperature 1400°C option
Radioactivity detector		Procter & Gamble, Cincinnati, OH, U.S.A.	See ref. 4
Liquid nitrogen dewar	LS-160	Union Carbide, Indianapolis, IN, U.S.A.	
Liquid nitrogen solenoid valve (3)	S74228A1	Automic Switch, Florham Park, NJ, U.S.A.	
Flow controllers (3)	HGC-290	Analabs, New Haven, CT, U.S.A.	0–10 cc/min range
Pressure regulators (2)	2-3778	Supelco, Bellefonte, PA, U.S.A.	2–60 p.s.i.
Digital thermometer	2160A-J	Omega Engineering, Stamford, CT, U.S.A.	

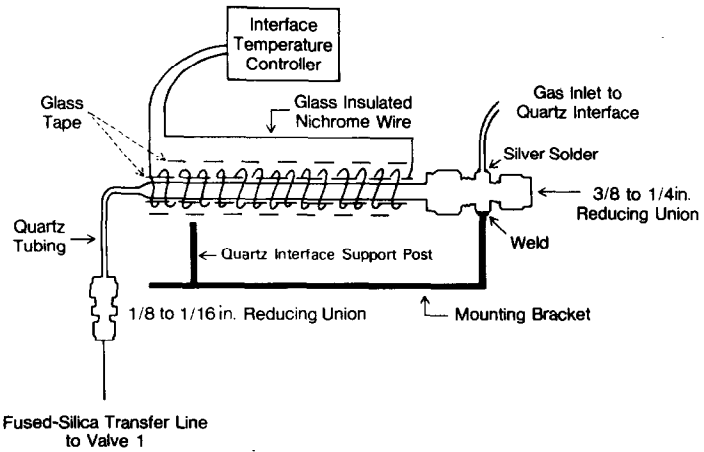

Fig. 1. Schematic diagram of the quartz thermal sampling interface.

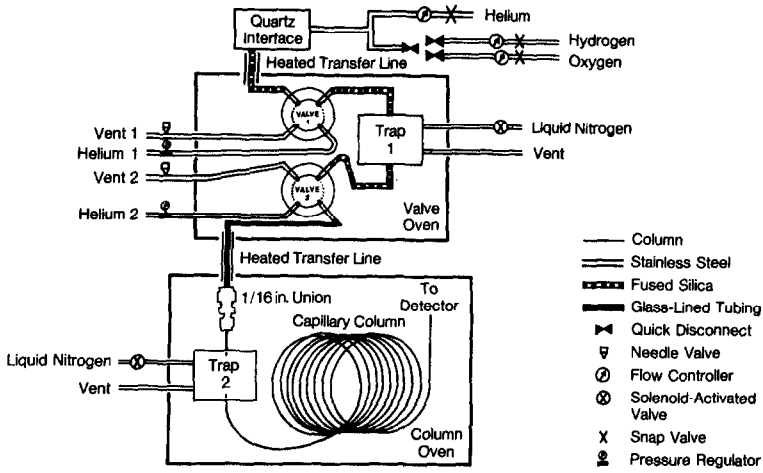

Fig. 2. Schematic diagram of the TSI, showing the quartz interface, valve oven, cryogenic traps, and GC column oven.

block was removed to make room for Trap 1. The construction of Trap 1 is shown schematically in Fig. 3. Machinable ceramic (Macor, Corning Glass Works, Corning, NY, U.S.A.) was used for the trap housing to permit operation at temperatures up to 350°C.

The transfer line between the valve oven and Trap 2 in the column oven was glass-lined stainless-steel tubing. This was placed inside a 2.5 in. (6.4 cm) × 1/2 in. (1.25 cm) I.D. copper tube wrapped with glass tape and nichrome wire.

Contact of the gas stream containing analyte components with active metal surfaces was significantly reduced by using all quartz, uncoated fused-silica capillary tubing, or glass-lined stainless-steel tubing. All vent lines and lines for make-up gases were 1/16-in. (0.16-cm) stainless-steel capillary tubing.

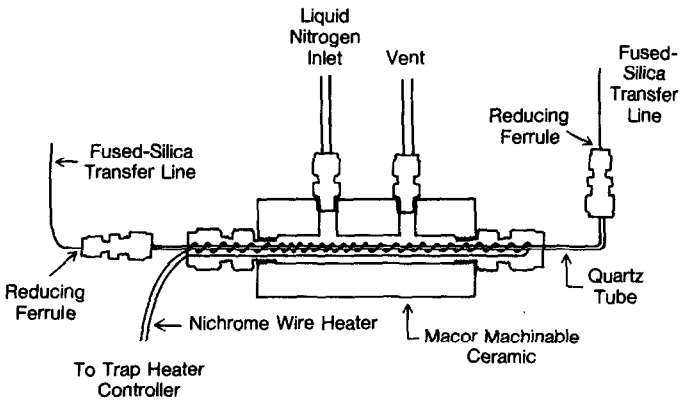

Fig. 3. Schematic diagram showing the construction of the cryogenic traps. Trap 1 uses a quartz tube as shown. In Trap 2, the quartz tube is replaced with a 1/16-in. O.D. (0.16-cm) stainless-steel tube. The fused-silica capillary column is placed inside the stainless-steel tube.

Precision needle valves (Series M, Nupro) were used to adjust the gas flow-rates out of Vents 1 and 2 under the constant pressure from Helium 1 and 2 (Fig. 2). The liquid nitrogen lines for cooling Trap 1 passed through the top of the valve oven.

The built-in heaters on the HP-5880 valve oven are insufficient to maintain a uniform temperature within the valve oven even when liquid nitrogen is not being used to cool Trap 1. To overcome this problem, air preheated to 250°C with an external heater is continuously introduced into the valve oven.

Trap temperature controller. An electronic controller (Fig. 4) was designed to control the resistive heating and cryogenic cooling of both Traps 1 and 2. The signal from a thermocouple is amplified (741, Analog Devices) and compared (111, Analog Devices) with a setpoint voltage that corresponds to the temperature required. The liquid nitrogen solenoid valves or heater variacs are switched with solid state relays (D1210, Crydom) driven by the comparator electronics. The heating and cooling of the traps is enabled by contact closures on the external events option of the HP-5880.

The a.c. voltages applied to the cryogenic traps' resistive heating wires by the temperature controller were adjusted so that the traps' heating rates were *ca.* 16°C/sec. Therefore, the traps are heated from −125°C to 200°C in 20 sec.

Modifications to gas chromatograph. The liquid nitrogen solenoid valves were mounted on the exterior left side of the HP-5880. Both traps and the cryogenic column oven were supplied with liquid nitrogen from the 160 l liquid nitrogen dewar.

Trap 2 was mounted inside the column oven on the left side. Liquid nitrogen lines, heater and thermocouple wires for Trap 2 pass through the left column oven wall. Trap 2 is similar to Trap 1 except a 1/16 in. (0.16 cm) O.D. × 0.03 in. (0.76 mm) I.D. stainless-steel tube is used in place of the quartz tube. The fused-silica

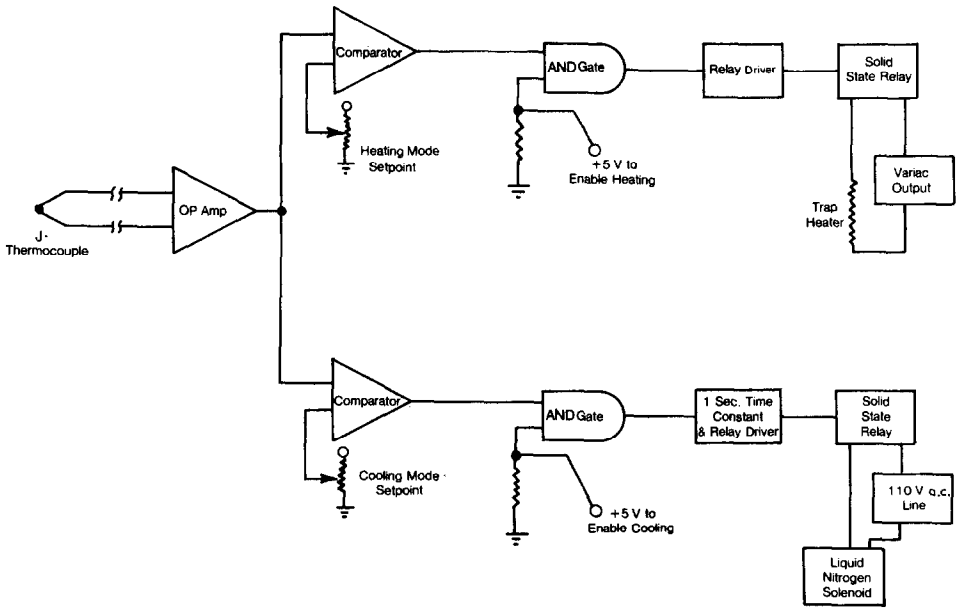

Fig. 4. Block diagram of the electronic controller designed to regulate the heating and cooling of both cryogenic traps.

TABLE II

EXTERNAL EVENTS CONTROLLED BY THE HP-5880

HP-valve number	*Function*
1	Valve actuator 1
2	Valve actuator 2
3	Extra
4	Extra
5	Capillary injection splitter valve
6	Bell used to signal analyst
7	Trap 1 heating ENABLE
8	Trap 1 cooling ENABLE
9	Trap 2 heating ENABLE
10	Trap 2 cooling ENABLE
11	Quartz interface heater ENABLE
12	Start pyroprobe temperature program

capillary column is placed inside the stainless-steel tube. Compounds transferred from Trap 1 are reconcentrated at the head of the chromatographic column by Trap 2 to maximize the column efficiency.

The transfer line from the column oven to a gas chromatographic radioactivity detector was made from 1/8-in. (0.32-cm) copper tubing that was wrapped with glass electrical tape, glass insulated nichrome wire, and glass wool insulation to minimize heat loss. This line passes through a hole drilled in the lower right side of the column oven. The transfer line is a section of uncoated fused-silica capillary tubing and is placed inside the heated copper line.

The automation of the thermal sampling experiment is controlled with the HP-5880 external events option. The functions of the twelve event positions are summarized in Table II.

Modifications of CDS pyroprobe. The CDS pyroprobe was used in this work because it meets several of our needs. The temperature is easily selected over a wide temperature range. The unit is commercially available and readily interfaced to a gas chromatograph.

It is difficult to make repeated gas-tight connections between the pyroprobe shaft and the injection port using the septum "O-ring" seal provided by the manufacturer. This problem was solved by replacing the CDS aluminum collar and septum seal with a 1/4-in. Swagelok nut and 1/4-in. one-piece PTFE ferrule. The gas-tight connection between the quartz interface and pyroprobe is easily made. The continuous bleed of organics from the septum seals of the pyroprobe caused a high and unacceptable background in the chromatogram. The use of PTFE ferrules to seal the pyroprobe eliminates this large organic contamination.

The pyroprobe is remotely triggered by the HP-5880 using the remote start connection of the CDS pyroprobe electronics module.

Instrument characterization

Typical experimental operating conditions of the TSI are given in Table III.

After the gas chromatograph was modified to perform the thermal sampling

TABLE III

TYPICAL EXPERIMENTAL OPERATING CONDITIONS OF THE THERMAL SAMPLING INSTRUMENT

Temperature	
Interface: initial (stand-by)	28–60°C
sampling	Ambient–300°C
interface to Trap-1 transfer line	220°C
Valve oven	220°C
Trap 1: cooling mode	−125°C
heating mode	210°C
Trap 2: cooling mode	−125°C
heating mode	200°C
Valve oven to GC transfer line:	220°C
Gas flow	
Helium 1:	15 p.s.i.
Helium 2:	12 p.s.i.
Atmosphere (helium):	10 ml/min
Chromatographic	
Columns:	Typically fused-silica capillary temperature programmed, as noted

experiments, we needed to ensure quantitative trapping and transfer of thermally evolved compounds through the system. We chose several ^{14}C-radiolabelled compounds as models to study the system's transfer efficiencies. Pentane solutions of [^{14}C]dibromomethane ($^{14}CBr_2$), [^{14}C]*n*-hexadecane ($^{14}C_{16}$), [^{14}C]propionic acid ($^{14}C_3$-acid), and [^{14}C]butyric acid ($^{14}C_4$-acid) were prepared. These were sequentially injected into the quartz interface using the solvent flush technique with 1 μl of pentane. A PTFE-faced septum (Microsep F-532, Canton Bio-Medical Products) was placed inside the 1/4-in. (0.64-cm) Swagelok nut (on the interface, Fig. 1) for liquid injections. No chromatographic column was used. The injected materials were trapped on Trap 1 and transferred through both high-temperature valves to the chromatographic column oven. A 5-cm section of blank fused-silica tubing was used to bubble the helium carrier gas containing the radiotagged compound into the scintillation cocktail. All samples were counted by conventional techniques and equipment (Packard Model 2001, Downers Grove, IL, U.S.A.).

The reproducibility of the TSI was demonstrated for the pyrolysis of polystyrene (PS), a polymer chosen for a model compound. Polystyrene (National Bureau of Standards, Washington, DC, U.S.A., No. 705) was dissolved in methylene chloride (1.01 μg PS/μl). A gas chromatographic syringe was used to deposit 5 μl of the PS standard solution onto the platinum ribbon of the pyroprobe. The polymer was pyrolyzed in helium using a heating rate of 20°C/msec from 65°C to 750°C. The ribbon was heated for a total of 10 sec. The evolved compounds were separated on a DB-1 fused-silica capillary column (15 m × 0.33 mm I.D., 0.25 μm film thickness, J&W Scientific, Rancho Cordova, CA, U.S.A.). The column was programmed from 50°C to 70°C at 2°C/min, then to 150°C at 10°C/min.

The residue of PS on the pyroprobe platinum filament was determined by repyrolyzing the sample without removing it from the interface between analyses. No additional degradation between analyses is expected, since the quartz interface is near

room temperature during this standby time. The absolute recovery of pyrolysis products of PS was determined using radiolabelled poly[8-^{14}C]styrene (^{14}C-PS, 538 μCi/g, Amersham International, Amersham, U.K.). A methylene chloride solution of ^{14}C-PS was prepared containing 5235 dpm per 2 μl, and 2 μl of the standard were applied to the platinum filament. The ^{14}C-PS was pyrolyzed from 60°C to 800°C at a heating rate of 20°C/msec in a helium atmosphere. No chromatographic column was used. The pyrolysis products successfully transferred to the column oven were trapped in a scintillation cocktail. After pyrolysis was completed, 5 cm of the filament end of the pyroprobe were directly rinsed in a scintillation cocktail. The quartz interface was mechanically washed with a cotton swab moistened with hexane or toluene. The cotton swab was rinsed in the scintillation cocktail. All samples were counted.

The linear range and detection limit for the pyrolysis of PS were determined using the same pyrolysis and GC conditions used for the reproducibility experiments. Standards of PS were prepared over the concentration range of 0.0101 μg/2 μl through 10.15 μg/2 μl using methylene chloride as the solvent. A GC syringe was used to apply 2 μl of the PS standards to the pyroprobe platinum filament using the solvent flush technique. These standards were repetitively pyrolyzed over a five-day period.

Applications. A method was developed to directly determine limonene in packaging materials. A small section of the packaging material (*ca.* 4 mg) was weighed and placed inside the quartz interface. The interface was heated rapidly to 175 ± 5°C to thermally desorb the limonene. The DB-1 fused-silica column was used for the separation of limonene from other compounds. The GC conditions were optimized for the resolution of limonene from other detected compounds, and for a rapid analysis. Therefore, compounds retained longer than limonene were rapidly eluted from the column using a temperature program rate of 30°C/min. The packaging materials were not pyrolyzed so that potentially interfering compounds were not generated.

The analysis of polyethylene vinyl acetate (PEVA) by pyrolysis is demonstrated. The pyrolysis products were separated on a Carbowax 20M fused-silica column (30 m × 0.32 mm I.D., 0.25 μm film, J&W Scientific). The samples were pyrolyzed on a platinum filament from 60°C to 650°C at a heating rate of 20°C/msec in a helium atmosphere.

The TSI can be used to emulate the thermogravimetric analysis (TGA) experiment. The mass rate of volatile evolution *vs.* temperature is measured as opposed to weight lost *vs.* temperature in the TGA experiment. This experiment can be performed with the TSI using sample weights of *ca.* 1–50 μg. A thermogram of ^{14}C-PS (20 μg, 11 nCi) using flame ionization and radioactivity detection was performed. The sample was heated in a helium atmosphere to 800°C at a heating rate of 10°C/min. The high-temperature valves were positioned so that the quartz interface was directly connected to the flame ionization detector using Trap 1 as a transfer line. No chromatographic column was used. The temperature experienced by the sample was calculated from the initial temperature, heating rate, and time.

RESULTS

Instrument characterization

The absolute recoveries of radiolabelled compounds injected into the TSI and

TABLE IV

ABSOLUTE RECOVERIES OF RADIOLABELLED COMPOUNDS INJECTED, TRAPPED, AND TRANSFERRED THROUGH THERMAL SAMPLING INSTRUMENT

Compound	*Mass (ng)*	*Recovery (%)*
[^{14}C]Dibromomethane	64 μg	93 ± 1
[^{14}C]*n*-hexadecane	12 ng	88 ± 6
[^{14}C]*n*-Propionic acid	2 ng	74 ± 5
[^{14}C]*n*-Butyric acid	4 ng	85 ± 4

collected in scintillation cocktails are shown in Table IV. The reproducibility of the TSI is illustrated in Fig. 5 for the pyrolysis of polystyrene in helium. The total peak area for all peaks detected was reproduced with a relative standard deviation (R.S.D.) of 4%. The peak area of styrene, the major component detected, was reproduced with an R.S.D. of 4%. All peaks with a peak area abundance over 0.01% were reproduced with an average R.S.D. of 9 ± 5%. The retention times of the peaks were reproduced to within ±1.1 sec between 0 and 18 min retention. Toluene and styrene were identified by comparison of retention index with those of analytical standards. Identification of other peaks was not possible since gas chromatography–mass spectrometry was not available on the TSI.

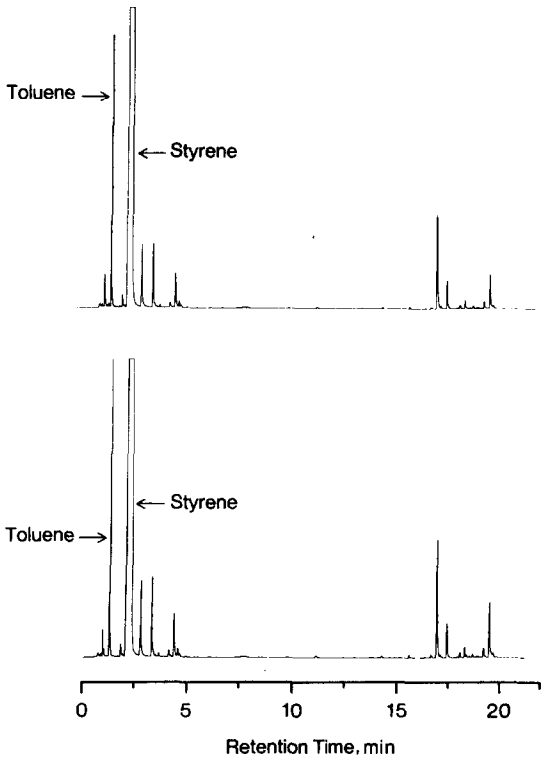

Fig. 5. Replicate pyrograms of polystyrene.

TABLE V

ABSOLUTE RECOVERY OF RADIOLABELLED PYROLYSIS PRODUCTS OF [^{14}C]POLYSTYRENE

Location	*Recovery (%)*			
	Run 1	*Run 2*	*Run 3*	*Average*
Vent 1: loss before pyrolysis	<0.1	–	–	<0.1
Vent 1: loss after pyrolysis	<0.1	–	–	<0.1
Vent 2: loss after pyrolysis	0.2	–	–	0.2
Transferred to GC column	69.8	65.0	69.8	68
Residue in quartz interface	3.1	2.9	3.3	3
Residue on end of pyroprobe	25.4	22.5	24.7	24
Total radiolabel recovery	98.5	90.4	97.8	95

The residue remaining on the pyroprobe from the second chromatogram in Fig. 5 was repyrolyzed. A small peak for styrene was detected corresponding to less than 2 ng or 0.04% of the original sample mass. Several early eluting peaks were detected before styrene. These peaks are representative of the organic background or contamination of the system.

The absolute recoveries of radiolabelled pyrolysis products of ^{14}C-PS are summarized in Table V. These results show the distribution of PS-derived compounds; for example, the percentage transferred to the GC column, the percentage lost by condensation onto the interface walls and the percentage remaining on the pyroprobe.

The plot of styrene peak area *vs.* mass of polystyrene applied to the pyroprobe filament is linear over the sample mass range of 1–12 μg. Sample masses above 12 μg were not evaluated, but linearity and chromatographic quality will be limited by the column capacity. The slope of the calibration curve changed with each decade change in sample mass. The slopes (styrene peak area per microgram of sample)

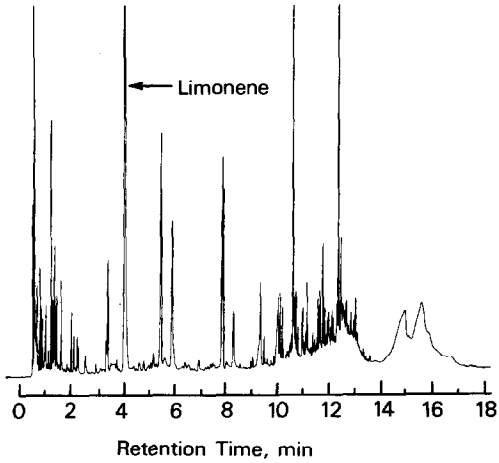

Fig. 6. Separation of thermally desorbed volatile compounds released from the packaging material sample.

between 1 and 12 μg, 0.1 and 1 μg, and 0.01 and 0.1 μg sample mass were 16,400, 10,200, and 220, respectively. The correlation coefficient for the linear fit between 1 and 12 μg was 0.998. The plot of toluene peak area *vs.* mass of polystyrene applied to the pyroprobe behaved similarly to that of styrene.

Applications

Fig. 6 is a chromatogram showing the separation of limonene from other thermally desorbed, volatile compounds released by a sample of a packaging material. The limonene level corresponds to *ca.* 25 ppm in the packaging material or 85 ng detected in the chromatogram. When the same piece of packaging material was re-analyzed immediately after the determination in Fig. 6, no additional limonene was detected, as seen in Fig. 7. The entire analysis, including thermal desorption, trapping of evolved compounds, and chromatography, is completed within 35 min.

Acetic acid was the primary volatile compound detected for the pyrolysis of PEVA in helium, as shown in Fig. 8. Acetic acid was identified by comparison of the retention index with that of an acetic acid standard. Acetic acid was detected with an R.S.D. of 10% at approximately the 200 ng level.

The use of the TSI to emulate the thermogravimetric analysis experiment is illustrated in Fig. 9. The generation and parallel detection by flame ionization detector and radioactivity detector of volatiles released during the decomposition of ^{14}C-PS begins at approximately 500°C and maximizes at 740°C. The evolution of radiolabelled decomposition products from ^{14}C-PS is confirmed with the radioactivity detector.

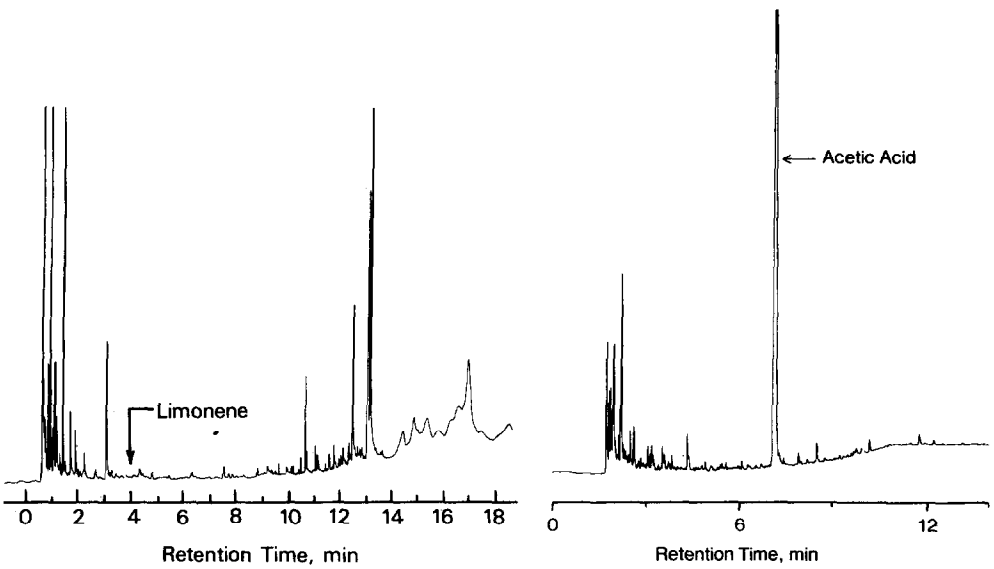

Fig. 7. Separation of thermally desorbed volatile compounds released from the packaging material sample previously analyzed in Fig. 6.

Fig. 8. Pyrogram of 1 μg of PEVA.

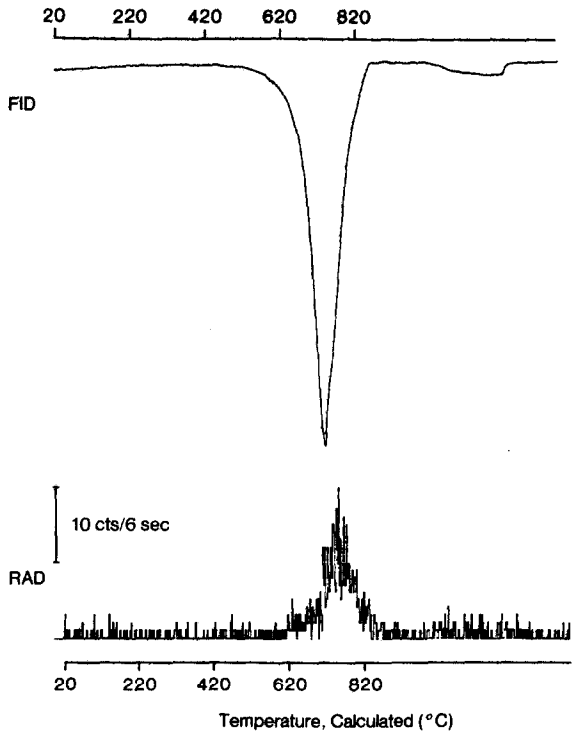

Fig. 9. Emulation of the TGA experiment using the TSI. Degradation of 20 μg (11 nCi) of [^{14}C]polystyrene. FID = Flame ionization detector; RAD = radioactivity detector; cts = counts.

DISCUSSION

The high absolute recovery of $^{14}CBr_2$ shows Trap 1 effectively condenses and retains compounds as volatile as dibromomethane. There are no major leaks or high-temperature valve malfunctions causing the loss of analyte. The amount of sampling atmosphere (here, helium) sweeping the quartz interface is sufficient to ensure transfer of the injected compound to Trap 1. There are no significant cold spots in the instrument's transfer lines and valve oven since $^{14}C_{16}$ was transferred with an absolute recovery of 88%. The absolute recoveries of $^{14}CBr_2$ and $^{14}C_{16}$ are not significantly affected by active surface sites in the valves and transfer lines since these are non-polar compounds. Therefore, these absolute recoveries are not a measure of the inertness of the transfer lines and valves.

The absolute recoveries of $^{14}C_3$-acid and $^{14}C_4$-acid at the 2–4 ng level are lower than the recoveries of the non-polar compounds. The free acids are very polar and have a high affinity for the surface. Only chromatographic systems with the inertness of the TSI can successfully transfer compounds of this polarity at the nanogram level.

The high degree of reproducibility of both peak area and retention time is possible only with an automated experiment. In our experience, it was not possible for an individual to accurately and repetitively switch instrument settings or valve positions from analysis to analysis.

The peak area of styrene, the major pyrolysis product of polystyrene, was reproduced to within 4%. This compares favorably with results from other experiments where the peak areas detected for repetitive injections of decane headspace were reproduced to better than 2% relative at the 50-ng level. Therefore, the TSI is capable of making measurements with a precision better than 5%. The actual precision of determinations can be worse than that if the precision becomes limited by the sample matrix. For example, the determination of sorbed compounds on a substrate will not be reproducible if the sorbed compound is very non-homogeneously distributed on the substrate.

The column is re-equilibrated with the carrier gas head pressure supplied by Helium 2 (Fig. 2) for 3–4 min after the compounds condensed in Trap 1 are transferred to Trap 2 and Valve 2 is switched to its normal position (solid line, Fig. 2). During the equilibration time, the carrier gas linear velocity is restored to that used during the separation process. This is necessary to ensure that the retention times of the peaks are reproduced. The carrier gas linear velocity increases during the transfer of compounds from Trap 1 to Trap 2 because Helium 1 pressure is slightly higher than the Helium 2 pressure.

The background derived from organic contaminants in the transfer line tubing, connections, valves, regulators, and other instrument components must be minimized. Organic contaminations will be significantly concentrated during the cryogenic trapping operations. We minimized organic contamination by washing all fittings and tubing with hexane, methylene chloride, and acetone. After the solvents were evaporated from the tubing using a helium flow, the tubing was heated with a propane torch. The helium carrier gas is purified by combusting the trace organics at 800°C in a stainless-steel tube packed with copper(II) oxide. As a result, less than 1 ng of organics is detected in a background run.

Over 99.9% of the PS sample applied to the pyroprobe filament was lost from the filament during pyrolysis. Initially, it might be concluded the entire sample applied to the filament was pyrolyzed and transferred to the chromatographic column. The experimental work with radiolabelled PS shows this apparent conclusion is incorrect.

Only 68% of the PS degradation products would be transferred to the chromatographic column, when one is used during an actual determination. Therefore, any mechanisms proposed to explain the thermal degradation of PS based upon the compounds identified and quantitated using the pyrogram would be inaccurate or incomplete. In practice, the problem is more complex since the chromatographic column could adsorb compounds, causing further inaccuracies.

Three percent of the radiolabel was found on the inside walls of the quartz interface. Therefore, the quartz interface is not responsible for a significant fraction of the loss of radiolabel.

The pyroprobe was found to contain 24% of the radiolabelled PS. This was surprising since no significant residue was found on the filament after unlabelled PS was pyrolyzed. Therefore, the loss of PS degradation products is to the stainless steel support holding the filament, not to the filament. This loss is totally independent of the TSI. The TSI quartz interface sweeps the filament area with helium significantly better than does the CDS quartz-lined interface. Most likely, the compound loss to the filament support is less severe with the TSI than with the CDS quartz-lined interface.

The total absolute recovery of all radiolabelled compounds derived during the pyrolysis of PS was 95%. Other losses of compounds to the TSI are minimal compared to the loss of 24% to the pyroprobe filament support. Since losses of evolved compounds are possible when other chemical systems or matrices are studied, the use of radiolabelled compounds to determine absolute analyte recoveries is suggested.

The build-up of organics on the pyroprobe can eventually lead to the formation of artifact peaks in pyrograms and to a significantly increased background. Before the application of a sample, the end of the pyroprobe is flamed with a propane torch to combust organic residues off of the pyroprobe.

The linear region of the evolution of styrene during the pyrolysis of PS also demonstrates the stability and repeatibility of the TSI over a one-week period. After initial calibration, it may only be necessary to run several standards, rather than complete calibration curves, during sample determinations performed over several days.

The surface effects of the platinum filament become discernible below the 1 μg PS level. As the mass of PS applied to the pyroprobe is decreased, the amount of styrene detected per mass unit of the polymer significantly decreased. Our system will not trap and retain compounds such as methane and ethane using trap temperatures of −125°C. When both cryogenic traps were operated at −165°C, the mass of low-molecular-weight compounds appeared to increase at lower sample weights of PS. We calculated that below *ca.* 100 ng, the sample approaches monolayer coverage on the pyroprobe filament. The catalytic effects of the platinum filament become more significant as we approach monolayer coverage, and cause significant destruction of the sample molecules to form low-molecular-weight compounds. These results are in agreement with Andersson and Ericsson[5], who demonstrated the decrease in yield of styrene from PS when less than 1 μg is pyrolyzed on a platinum filament.

Applications

The use of the TSI for the determination of thermally desorbable compounds from substrates is demonstrated by the analysis of limonene in packaging materials. The generation of compounds derived from the packaging materials that could interfere with the determination of limonene was minimized by heating the sample to only *ca.* 175°C. At this temperature, the packaging material was not pyrolyzed.

The quartz interface can be rapidly programmed to a temperature higher than the initial temperature. This is necessary to perform the thermal desorption experiment and to minimize or eliminate initial temperature artifacts during the Py–GC experiment. If the packaging material sample was placed into the interface preheated to 175°C, limonene would immediately desorb and be lost since the interface cannot be instantaneously sealed gas-tight. In our experiment, the sample is placed into the interface that is at room temperature (*ca.* 28°C). The interface is rapidly heated to 175°C only when the valves are properly positioned and Trap 1 is cooled. During the pyrolysis experiment, the interface temperature can be a compromise between a temperature low enough to prevent slow premature thermal degradation, and a temperature sufficiently high to prevent condensation of compounds evolved when the sample is pyrolyzed. The quartz interface is held at room temperature until 15 sec prior to beginning pyrolysis, and is then rapidly heated to a temperature high enough to prevent analyte condensation. Therefore, premature thermal degradation of the sample is minimized.

The TSI can perform analyses at trace levels. Since evolved compounds are cryogenically concentrated by the traps, the evolved compounds are transferred without splitting to the capillary column. Many other Py–capillary GC systems require using the capillary injection port in the splitting mode, thereby reducing sensitivity. Trace analysis can only be performed using cryogenic trapping and concentrating techniques when the system and carrier gases are ultra-clean, as in our system.

The inertness of the TSI is further demonstrated by the analysis of PEVA by pyrolysis to free acetic acid. Free carboxylic acids are extremely difficult to chromatograph due to their polarity and, hence, their interaction with surface active sites. This analysis could not be performed in our laboratories using direct Py–GC with packed columns at the concentration levels presented in this work.

The emulation of the TGA experiment provides important information about the sample being studied. The temperature at which thermal degradation begins is found. The experiment using the TSI can be performed using sample masses below one microgram. If selective detection is used, such as flame photometric, or mass spectrometry, information can be obtained about the chemical composition of the compounds evolved during the thermal degradation. The current limitation of this experiment is temperature calibration. The temperature axis shows calculated, not measured, temperatures. Methods for accurate temperature calibration are now being developed.

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