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Repetitive liquid injection system for inverse gas chromatography

S. Panda, Q. Bu, K.S. Yun, J.F. Parcher*

Chemistry Department, University of Mississippi, University, MS 38677, USA

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Abstract

A hybrid injection system composed of a closed-loop vaporization chamber with a gas sampling valve is described. The system allows liquid injection into the vaporization loop with subsequent multiple injections of the vaporized solute(s) via the gas sampling valve (GSV). Very small amounts of probe solutes can be injected without a dilution solvent, and the vaporization loop acts as a "retention gap" for capillary columns. The use of a pneumatically controlled valve injector provides very accurate and reproducible injection volumes at precise time intervals. Combination of precisely timed injections with temperature programming of the column oven produces continuous chromatograms and retention data at controlled temperature increments. The proposed injection system eliminates the need for split injectors; it is cleaner than normal in-line injectors because nonvolatile samples cannot reach the column; and the instrumentation is easily automated. The major disadvantages are the restriction that the samples must be volatile at temperatures lower than the upper temperature limit of the valve rotor; the GSV is susceptible to both contamination and mechanical failure; the sample can be exposed to metal components of the valve; and initial distribution of the sample throughout the closed-loop vaporization chamber may be slow.

1. Introduction

Inverse gas chromatography (IGC) is an established method for the investigation of surfaces and interfaces, as well as the study of polymer structures, interactions, and phase transitions [1]. The technique is based on the measurement of the retention behavior of one or more well-characterized probe solutes to determine some physical or chemical properties of nonvolatile stationary phase materials, such as polymers, solid adsorbents, or mixtures of materials. The usual experimentation involves the measurements of the retention volumes of the probe solutes over a range of temperatures. Thermodynamic parameters can be calculated directly from the retention data, and phase changes can often be detected from discontinuities in a van't Hoff-type plot of the logarithm of the retention volume versus the reciprocal temperature [2–6].

The experimental technique of IGC is very appealing because the material to be examined can be coated on a solid support (to provide a thin film) in a packed column or coated on the walls of an open tubular capillary column (to avoid the possibility of adsorption on a solid support). The experiments can be performed isothermally or in a temperature-programmed mode similar to differential scanning calorimetry (DSC) methodology. The samples can be in-

* Corresponding author.

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jected as vapors via a gas sampling valve (GSV) or by liquid syringe injections. The experiments are simple, fast, and require no specialized instrumentation. These are particularly significant advantages when compared to such alternative techniques as DSC. A variety of solutes can be used as probes to study different types of molecular interactions in a low-energy regime that is difficult to investigate by classical experimental techniques. Finally, the technique can be applied to systems not amenable to other experimental approaches. For example, IGC can be used to study phase transitions in polymers in contact with sorbable vapors or supercritical fluids at high pressures.

Nevertheless, there are some problems associated with the technique of inverse gas chromatography. Most of the difficulties arise from the complexity of retention mechanisms typically observed with IGC systems. Solute adsorption on polymeric surfaces is usually prevalent, and concurrent bulk partition mechanisms are often observed, the relative significance of which may depend upon the temperature and the state of the stationary phase. Adsorption mechanisms are usually complicated, resulting in nonlinear isotherms especially at low temperatures, and both adsorption and partition (diffusion) kinetics may be slow on a chromatographic time scale. As a result of these problems, elution peaks for the probe solutes are often asymmetric and retention volumes may consequently vary with sample size, film thickness, and often with flow-rate as well. These phenomena are usually observed with polymeric materials at temperatures close to the glass transition temperature, T_g, of the stationary phase.

Another problem is often encountered in the interpretation of the van't Hoff plots used to determine phase transition temperatures. Such interpretation is complicated by nonequilibrium conditions observed when the stationary phase undergoes a phase transition. Under these conditions, solute retention mechanisms almost always include both adsorption and partition, which may be influenced by slow diffusion kinetics. Thus, the flow-rate of the carrier gas, which determines the contact time of a solute with the stationary phase, becomes a critical parameter. Some authors have suggested extrapolation of the retention volumes at a fixed temperature to zero flow-rate to measure (equilibrium) partition and adsorption [5,6]; whereas others [3] have proposed the opposite extrapolation to infinite flow-rate to eliminate retention contributions from partition mechanisms. Determination of transition temperatures from van't Hoff plots is further complicated by the assignment of such transition temperatures to local maxima, i.e., the first deviation from linearity with decreasing temperature, in some systems (liquid crystalline polymers [2], for example). In other cases, local minima, i.e., the first deviation from linearity with increasing temperature, are used to locate the transition temperature(s) (polystyrene [5,6] is an example).

Investigation and resolution of these problems are critically dependent upon reliable experimental data from IGC experiments. In turn, the integrity of the experimental technique is dependent upon an accurate delivery system for the probe solute(s). The injection system must provide multiple injections of equal amounts of the same sample at precisely controlled time intervals. The injected volumes must be small to ensure infinite dilution conditions; however, any solvent, such as those commonly used to dilute analytical samples, is undesirable because a large solvent peak could limit the cycle time for repetitive injections and/or obscure early eluting solutes. Syringe injections of liquid solutes (with and without solvent) have been used for IGC studies; vapor injection has also been used and is an excellent injection method but limited to volatile solutes; and automatic liquid samplers (ALSs) [8] as well as head-space injectors [2,4] have all been used for IGC studies. Syringe injections of liquids or vapors, whether manual or with an ALS, are seldom adequately reproducible, especially with split injector systems. Head-space injectors and GSVs are more reproducible but limited to volatile solutes. None of these injection methods is entirely satisfactory. Thus, in an attempt to alleviate at least

some of these problems, a hybrid injector system involving injection of vaporized liquid samples via a gas sampling valve is described herein.

2. Experimental

The proposed injection system is illustrated schematically in Fig. 1. The packed-column injector, gas sampling valve, and isolation valve must all be maintained at a temperature sufficient to assure complete vaporization of all probe solutes but below the upper temperature limit of the GSV rotor (typically 350°C). In Fig. 1, the sampling valve is shown in a dual-injection mode because this configuration allows the maximum number of injections from an event table in a typical GC–MS system. However, a normal six-port valve with a single injection loop would work as well. In an injection sequence, the isolation valve would be set in the position shown in Fig. 1 to form a closed loop (shown in bold) with the injection port and GSV. A liquid sample can be injected into the packed-column injector and allowed to vaporize and distribute throughout the closed loop. Individual injections into the analytical column are initiated from the sampling valve at fixed time intervals. In this particular instrument, the capillary inlet system was used simply as a splitter in front of the mass specific detector. The capillary column was maintained at a sufficiently high temperature to act merely as a transfer tube rather than a separation column. If this is not feasible, the capillary column can be replaced with an empty fused-silica column. At the completion of an injection sequence, the vaporized sample can be removed from the injector by actuating the isolation valve to allow a sweep gas to flush out the analytical sample.

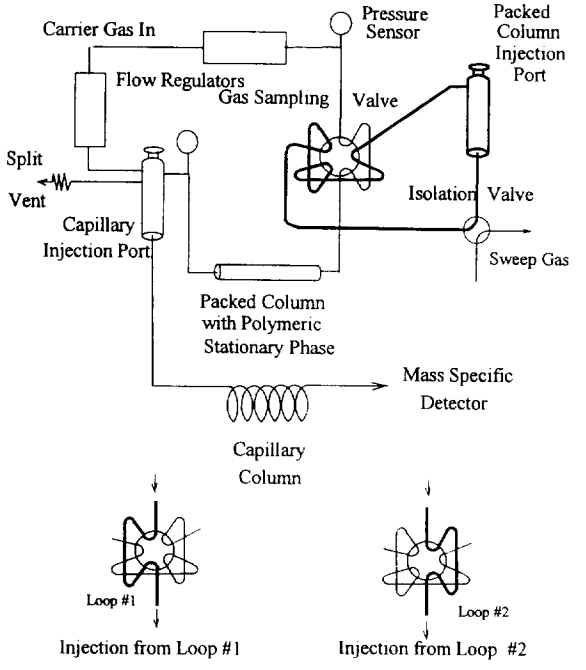

Fig. 1. Schematic diagram of the off-line IGC injection system.

In this investigation a mass specific detector was used as the detection device, although any GC detector would be acceptable. The advantage of a mass specific detector for IGC experiments is the ability of this detector to distinguish individual probe species even if they are not chromatographically resolved from other species or a solvent peak.

3. Results and discussion

Typical IGC data collected with the injector system described previously are shown in Fig. 2. In this example, the polymer was polymethylmethacrylate (PMMA) and the probe solute was xylene. The literature value [9] for the glass transition temperature, T_g, of PMMA is about 105°C. The column temperature was programmed from 50 to 220°C at 1°C/min during the course of the experiment. The valve injector was programmed for repetitive injections at 10-min intervals. This sequence produced elution peaks at approximately 10°C intervals. The period is not precise because the retention times of the probe solutes varied significantly with temperature and the physical state of the polymer.

The measured retention volume data for xylene with PMMA are shown in Fig. 3 in the

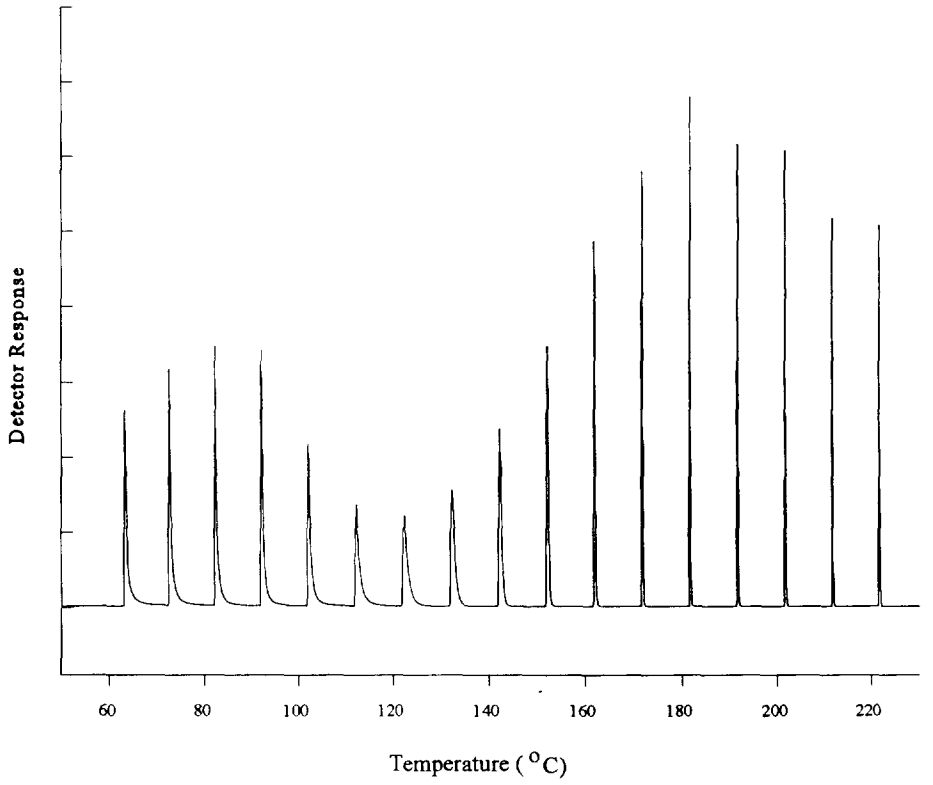

Fig. 2. Chromatogram of xylene on PMMA with the column temperature programmed from 50 to 220°C at 1°C/min.

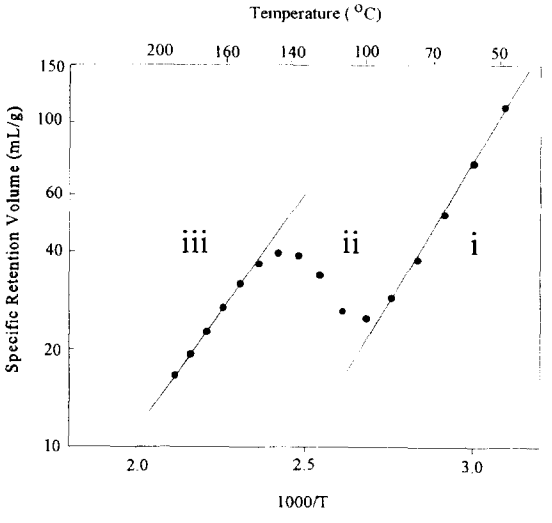

Fig. 3. Van't Hoff plot for xylene with PMMA polymer.

form of a classical van't Hoff type plot of $\ln V_g^0$ versus $1000/T$. The generally accepted interpretation of such plots involves division of the plot into three distinct regimes. These are (i) the linear region at low temperatures that typifies the glassy phase of the polymer and the slope of the line is proportional to the enthalpy of adsorption of the probe solute on the surface of the polymer film, (ii) the discontinuity at intermediate temperatures reflecting a nonequilibrium condition in which the retention of the probe depends on the contact time of the probe with the polymer surface, and (iii) the second linear portion at high temperature where the polymer state is rubber and the slope of the line reflects the enthalpy of solution of the probe solute in the bulk polymer. The exact retention mechanism for polymers in a rubber state is

uncertain, and it has been suggested that, even at high temperatures, the primary retention mechanism is surface adsorption [10]. The relative significance of adsorption and absorption mechanisms for polymers above T_g is probably determined primarily by the nature of the probe and the polymer and may vary significantly from one system to another.

Determination of T_g from inverse gas chromatography data such as that illustrated in Fig. 3 is somewhat problematical; however, the most common approach [5,6] is to specify T_g as the temperature at which the first deviation from linearity is observed in the low-temperature regime. In the example shown in Fig. 3, the T_g value calculated this way would be 90–100°C. In other cases, the phase transition temperature has been assigned as the temperature at the first point of deviation from linearity of the high-temperature region. Thus, T_g would be 140–150°C in the example shown in Fig. 3. Differential scanning calorimetric results, on the other hand, clearly show that there is a phase transition in the temperature range of 90–100°C, which shows that T_g should be determined from the point of deviation from linearity in the low-temperature range in this particular case.

3.1. Sample discrimination

The upper limit on molecular mass of the samples depends upon the temperature of the closed-loop injector. The upper temperature limit is usually set by the rotor of the GSV, and 350°C is a typical value. Thus, the proposed injection system is limited to solutes that have a reasonable vapor pressure at 300–350°C. This is a significant limitation for its use as a general injection system; however, most solutes used as IGC probes easily meet this requirement.

3.2. Dilution effects

The injection system is a closed loop, and the sample loop of the GSV is filled with carrier gas at the end of an injection cycle. Thus, a fixed volume of sample is lost with each injection and a similar volume of carrier gas is introduced into the closed-loop injection system. This results in a decrease in peak area with each successive sampling valve injection. A logarithmic plot of the normalized peak area versus injection number is shown in Fig. 4 for three commonly used IGC probe solutes. The slope of the regression line, which is equal to the log of the fraction of sample remaining in the closed-loop injector after each valve injection, was −0.014. Thus, a loss of about 3% of the sample per injection was observed for this particular system. The percentage loss will vary with the design of the systems and the volume of the sample loops in relation to the total volume of the closed-loop injector. Nevertheless, the loss of 3% per injection allows about 75 repetitive injections before the sample size is reduced to 10% of the original liquid sample injected into the packed column inlet. The relative standard deviation of the data shown in Fig. 4 was approximately 1.8%. This uncertainty included the variance due to the injector valve as well as the uncertainty in the integration measurements.

3.3. Peak shape analysis

The dilution effect described above produced elution peaks of decreasing peak area and, presumably, the peak heights should decrease

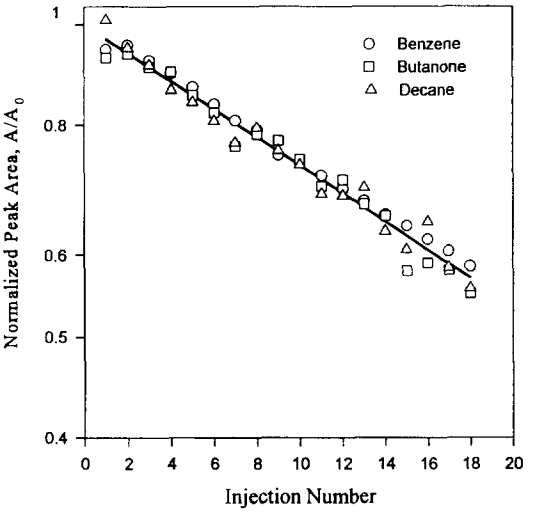

Fig. 4. Dilution effect caused by the gas sampling valve.

with an increasing number of injections. In fact, the chromatogram displayed in Fig. 2 shows that no such simple pattern is observed. Instead, a complex series of maxima and minima is evident throughout the chromatogram. This phenomenon is caused by an interdependent set of factors that each influence the shape of the elution peaks. These factors and their possible consequences are:

(1) The PMMA polymer undergoes a phase change from glass→rubber in the range of 90 to 100°C. As a result, the retention mechanism changes from predominately adsorption for the glassy polymer to primarily absorption in the rubbery or liquid polymer at high temperatures. Adsorption mechanisms usually produce asymmetric peaks, whereas absorption mechanisms produce Gaussian peaks if diffusion of the probe solute in the polymer is fast on the chromatographic time scale.

(2) The column temperature was programmed up with each successive injection. Such a temperature increase would normally produce increasingly sharp elution peaks with increasing height due to more efficient mass transfer kinetics in the polymer at high temperatures.

(3) The dilution effect causes the peak area to decrease with each successive injection. This would normally produce a concomitant decrease in peak height.

These factors, viz., temperature, phase change, dilution, absorption, adsorption, and diffusion, all affect the shape of the elution peaks shown in Fig. 2. Asymmetric peaks were observed below 120–130°C, whereas above 130°C the elution peaks were Gaussian (symmetric) with increasingly smaller band widths. In the temperature range 90–120°C, which encompasses the glass transition temperature, the peaks became increasingly broad with increasing temperature. This is an anomalous phenomenon rarely observed in chromatographic systems. The dispersion process (peak broadening) is enhanced due to the change in phase and slow mass transport in the rubber polymer at temperatures slightly above T_g. This pattern of peak shapes has been observed previously [7,11], and the explanation given above (excluding the dilution effect) is derived in part from the discussion therein. The relationship between retention, peak shape, and temperature is shown in Fig. 5, in which the logarithm of the specific retention volume of xylene is plotted versus the elution temperature of each peak. Superposition of the chromatogram (Fig. 2) and specific retention volume data (Fig. 3) illustrates the close correlation of the minimum in the pseudo-van't Hoff plot and the maximum peak spreading (minimum peak height) in the chromatogram. Continuous, precisely timed injections coupled with temperature programming of the column temperature are required for this type of investigation.

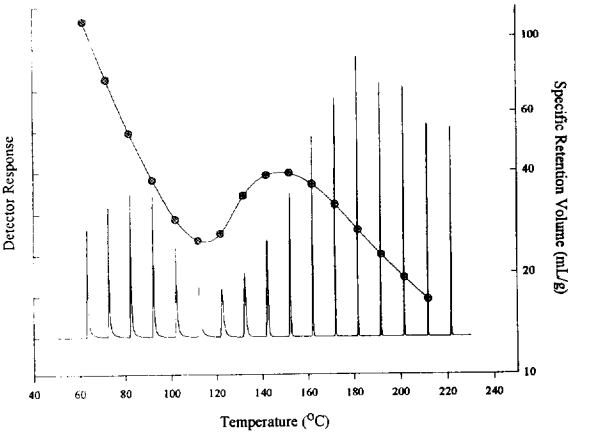

Fig. 5. Superposition of the chromatogram and specific retention volumes of xylene with PMMA.

3.4. Potential advantages of the injection system

The proposed system eliminates the need for flow splitting and retention gaps for capillary GC. Because the vaporization process occurs off-line, there are no flow or pressure disturbances and the cooling effect of the solvent vaporization does not influence the injections. The off-line injection system is cleaner and less susceptible to septum bleed or leaks than common in-line injectors. Nonvolatile sample components cannot contaminate the column but remain mostly in the liner of the packed-column injection port. Finally, the entire system is easily automated and very simple to operate.

3.5. Potential disadvantages

The system will be ineffective for very high boiling compounds because of the upper temperature limit of the gas sampling valve components. Because the GSV is a mechanical apparatus, it is subject to contamination, mechanical failure, and could cause catalytic reactions of some solutes. The device does not deliver a constant amount of sample due to dilution of the original sample with carrier gas by the GSV. Because the liquid sample is injected at only one point in the closed-loop system, a finite amount of time is required to achieve uniform distribution of the sample throughout the system. This time requirement varies with the design of the system as well as the type of sample.

4. Conclusions

While the proposed injection system is not a universal injector, it is an excellent device for repetitive injection of simple solute mixtures. Thermodynamic studies and inverse GC provide two examples of experimental techniques requiring such injection sequences. The system is simple, accurate, and easily automated. It requires computer control and remotely actuated valves; however, it can sometimes be used to replace split-flow injectors, eliminate septum purge flows, and retention gap technology.

Acknowledgements

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