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TRACER PULSE CHROMATOGRAPHY: A REVIEW AND PROSPECTUS

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CONTENTS

1. INTRODUCTION

Tracer pulse chromatography is a unique form of chromatography which has been in use almost twenty years, but is still relatively obscure compared to the other forms of chromatography. Part of the reason for this is that the technique is not really a separation method at all, but rather a method for measuring phase distribution equilibria. It is usually classed as a chromatographic technique because the procedures and instrumentation are identical with those used for the more conventional forms of chromatography.

In this review, the basic technique and capabilities of this unusual procedure will be discussed, including a relative comparison with alternative methods (both static and chromatographic) for measuring phase equilibria. Several practical applications will be presented and the review will conclude with a look at the future possibilities for significant new applications and further developments of this technique.

1.1. Adsorbate systems

The primary distinguishing feature of tracer pulse chromatography is that *the adsorbate is used as the carrier gas or as a component of the carrier gas*. Methane[1-11],

ethane[4,5,7,12,13], ethylene[13], propane[1,3,14,15], carbon dioxide[10,14], and other light gases[11,14] have all been used as carrier gases (adsorbates) for tracer pulse investigations. These gases are obvious choices for carrier gases; however, n-heptane has also been used with a liquid feed system coupled to a vaporization chamber[2]. Mixtures of sorbable gases[1,3,4,7,10,14] and mixtures of these gases with inert (nonsorbable) gases[15–17] have also been used with excellent results. No attempt has yet been made to correct the experimental data for gas phase nonideality; however, this can be readily accomplished when the accuracy and precision of the method have been improved to the point that the gas phase correction terms are justified.

1.2. Sorbent systems

The adsorbent is used as the stationary phase in a conventional packed gas chromatographic column. Historically, the classical solid inorganic adsorbents, such as silica gel, glass, molecular sieves, and charcoal, were first used for investigation of gas–solid adsorption equilibria by tracer pulse techniques. However, the technique is not limited to this type of adsorbent. The only critical requirements for the stationary phase are that it must be chemically and physically stable (unreactive and non-volatile) and that the kinetics of the phase transfer process must be rapid compared to the flow-rate of the mobile phase. Liquids, such as n-octane, n-hexadecane, and other high-molecular-weight alkanes, have been used extensively and partition isotherms for both ideal and non-ideal gas–liquid systems have been measured over a range of pressures and concentrations. There is no restriction on the number of components or phases for the sorbent(s) and both mixed liquids and liquid-modified solid adsorbents have been investigated.

1.3. Solute systems

Another unique feature of tracer pulse methods is that the primary experimental parameter is the retention time of a solute which is a distinguishable isotope of the adsorbate. Both stable (^{13}C and ^{2}H) and radioactive (^{14}C and ^{3}H) isotopes have been used to label these solutes. The isotopic solute must be chemically equivalent to the adsorbate-carrier gas, but distinguishable by some selective detector such as an ion chamber, scintillation counter, or mass spectrometer.

The isotopic solutes are injected as infinitely dilute elution samples as in normal gas–liquid chromatography. The retention time of the solute (or solutes for multi-component systems) must be "corrected" for the dead-time or retention time of a hypothetical unretained solute, and this sometimes requires a second detection system to measure the retention times of a series of inert gases or n-alkanes.

2. THEORY OF TRACER PULSE CHROMATOGRAPHY

The basic theory and mass balance equations have been derived many times in many different ways[3,18–20]. A striking feature of the mathematics is its extreme simplicity compared to the complex differential equations required to describe any other form of finite concentration chromatography, even the closely related "concentration pulse", "step-and-pulse", "elution-on-a-plateau", or "vacancy" chromatography.

The basic equation for the tracer pulse method is

$$n_i^{ads} = P_T Y_i V_{Ri}/RT_c \tag{1}$$

where n_i^{ads} is the amount (moles) of adsorbate i on (in) the stationary phase(s), P_T is the mean column pressure, Y_i is the gas phase mole fraction of component i, V_{Ri}^r is the corrected retention volume of. he labeled, isotopic adsorbate sample, R is the gas constant, and T_c is the temperature of the chromatographic column. This equation is valid whether component i is pure or a component of a mixture in either the mobile or stationary phase(s). This simple, yet elegant, equation can be derived directly from mass balance considerations with very few simplifying assumptions. Some of the necessary assumptions are (i) that the pressure of the isotopic solute is very low relative to the pressure of the adsorbate at every point in the column, (ii) that the pressure drop across the column is low, and (iii) that the system is at local equilibrium. Another assumption often used, but not theoretically necessary, is that the phase distribution of the labeled and unlabeled solute are identical, *i.e.*, that V_{Ri}^r for the labeled solute is the same as for the unlabeled form. under all the experimental conditions.

The experimental parameters that must be controlled are exactly the same as for elution gas chromatography, *viz.*, temperature, pressure, and flow-rate. The pressure and temperature limits are set only by the instrumental capacity. The measured variables are the same plus the retention times of the isotopic solute(s) and an "unretained" solute. In many cases. the retention time of helium, neon, nitrogen, or even methane can be used as a sufficiently accurate value for the dead-time. In other cases, especially if the retention time of the labeled solute is low, a mathematical extrapolation or linearization scheme must be used to evaluate this parameter. This procedure is not unique to tracer pulse methods and has been discussed extensively in the literature[5,6,12,21].

3. COMPARISON WITH ALTERNATIVE TECHNIQUES

3.1. Volumetric and gravimetric methods

The classical static methods for the determination of equilibrium isotherms are well established and have been shown to be accurate and applicable to sometimes incredible pressures. The primary disadvantage of the static methods compared to the dynamic (chromatographic) methods is the relatively long equilibration times required. This time is often measured in hours per data point. This can be reduced to minutes per point in a flow system with a packed bed adsorbent, such as a chromatographic column. The static methods are also somewhat limited in applications involving low concentrations of one or more components in either phase.

The major advantages of the static methods are the ability to cover wide pressure ranges and handle multicomponent systems and volatile or corrosive materials.

3.2. Other chromatographic methods

Normal elution gas chromatography has been used very successfully to measure phase equilibrium data for gas–solid, gas–liquid, and even gas–liquid–solid systems *for binary systems with linear isotherms*. This covers a wide range of material, but most real systems are non-linear at finite pressures. These are the systems of interest, and some form of finite concentration chromatography must be used to study these non-linear systems. There are several forms of frontal chromatography which have been used with varying success for phase quilibria studies. These methods

have been extensively reviewed and compared in the literature, and only the common points will be discussed.

The major advantages of any chromatographic system (including tracer pulse methods) are speed, accuracy, and simplicity. One disadvantage of the other chromatographic techniques is that the mathematical analysis is very complex for non-linear, and especially multicomponent, systems. Eqn. 1 must be expressed in a differential form with a derivative for one component multiplied by the concentration of the other component in any retention volume equation. This means that generation of an equilibrium isotherm is complex and usually involves a multiparameter curve fitting procedure of some kind.

Tracer pulse chromatography, on the other hand, is mathematically simple and generates a point on the isotherm directly for each experiment. The major disadvantages are the procurement, handling, and detection of the radioactive isotopes or the requirement for a complex, expensive mass spectrometer for the detection of the stable isotopes. Another problem with any chromatographic procedure is that there must be a pressure drop across the chromatographic system. The equilibrium distribution at the head of the column may differ from that at the outlet, and any data obtained must be an "average" value. This is a disadvantage but not a severe one and the technique has been shown to be accurate with relatively high pressure drops.

4. APPLICATIONS

4.1. Gas–solid adsorption studies

Tracer pulse chromatography was first used to measure adsorption isotherms of methane and propane on silica gel[1]. In addition, several mixtures of these gases were used to generate binary isotherms. Since then, numerous systems of this type have been investigated, including alkanes on silica gel[1,3-5], Porapak P and Q[11,12], Porasil[7,9], charcoal[2], molecular sieves[14], and graphitized carbon blacks (GCBs)[15-17]. Pressures up to 100 atm have been used routinely and, in many cases, both total adsorption of mixtures and individual component isotherms were determined.

Tracer pulse chromatography has not yet been used to determine gas–solid isotherms more complex than binary; however, there is no theoretical reason that ternary or even higher systems could not be studied by this method. The experimental difficulties are significantly increased for multicomponent systems. This is true for both static and chromatographic procedures; however, even for complex systems, the tracer pulse methods are simpler than others and eqn. 1 is valid for each component in the system.

4.2. Gas–liquid solution studies

Only a limited number of gas–liquid systems have been studied by this method because these systems are often amenable to other experimental procedures, especially gas–liquid chromatography if the systems follow Henry's law over a range of pressure. Only n-octane[6,8,10], n-hexadecane[13], and Carbowax 1500[16,17] (CW 1500) have been used to date; however, one of these studies[13] established the accuracy of the procedure by comparison of solubility data for carbon dioxide and propane in hexadecane with literature data over a range of temperatures. This type of comparison has also been carried out for methane in n-octane and the tracer pulse data were

shown to be in good agreement with previous studies[10]. These investigations also emphasized another unique application of tracer pulse methods, that is the measurement of the solubility of a probe solute —which is usually, although not necessarily, at infinite dilution, (pressure, $P \rightarrow 0$)— as a function of the composition of the binary (methane + octane)[8] or even ternary (methane + carbon dioxide + octane)[10] liquid phase. This type of experiment is very significant and almost impossible to carry out any other way with both volatile and non-volatile components in the stationary phase.

Solution isotherms of only one polar component (acetone) have been measured by tracer pulse methods. However, the solvents used represented two special types of liquids encountered in phase equilibrium studies. One (n-hexadecane) was a pure, well characterized liquid which was used for thermodynamic studies, i.e., activity coefficient vs. composition data. The other (CW 1500) was a poorly defined polymer (or worse, a mixture of polymers); however, equilibrium isotherms still yielded valuable information. One example was the study of the liquid $\rightarrow$ wax phase transition observed for CW 1500 at about 40°C. The tracer pulse method is identical for solid, wax, or liquid sorbents and can be used to follow a system through a phase change. This type of investigation has been carried out for CW 1500 present as a monolayer on the surface of a graphite adsorbent. It was observed that the transition temperature for the monolayer liquid was at least 15°C higher than for the bulk liquid.

4.3. Liquid-modified and vapor-modified adsorbents

Several recent investigations have centered on solid adsorbents, in particular GCBs coated with a monolayer or less of a non-volatile liquid or volatile vapor. The surface modifiers sometimes have a tremendous effect upon the adsorption properties of the adsorbent. Some modifiers block particularly strong adsorption sites on the surface to produce a surface which is effectively more homogeneous, less adsorptive, and has less capacity than the unmodified surface. Other modifiers, or even the same modifiers with different adsorbates, have the opposite effect and cause enhanced adsorption presumably due to lateral interactions on the adsorbent surface[15-17]. Fig. 1 is a plot of the retention volume of a small sample of propane on two GCBs as a function of the amount of butane adsorbed on the surface. This figure illustrates the tremendous effect that an adsorbed component can have upon the retention (adsorption) of a second component[16].

5. POTENTIAL APPLICATIONS FOR TRACER PULSE METHODS

The study of multicomponent phase equilibrium systems is probably the most promising area in which tracer pulse chromatography can be used to its full advantage. The study of "two-dimensional" chemical and physical processes which take place among adsorbates on a surface is a significant area which is difficult to study experimentally, expecially for systems with several components and/or phases. Tracer pulse chromatography is ideally suited for this type of investigation, especially with mass spectrometric detection. The mass specific detector can follow multiple components with sufficient speed to accurately determine the retention time of the peak maximum for each foreign component of labeled isotopic adsorbate-carrier gas in a complex mixture.
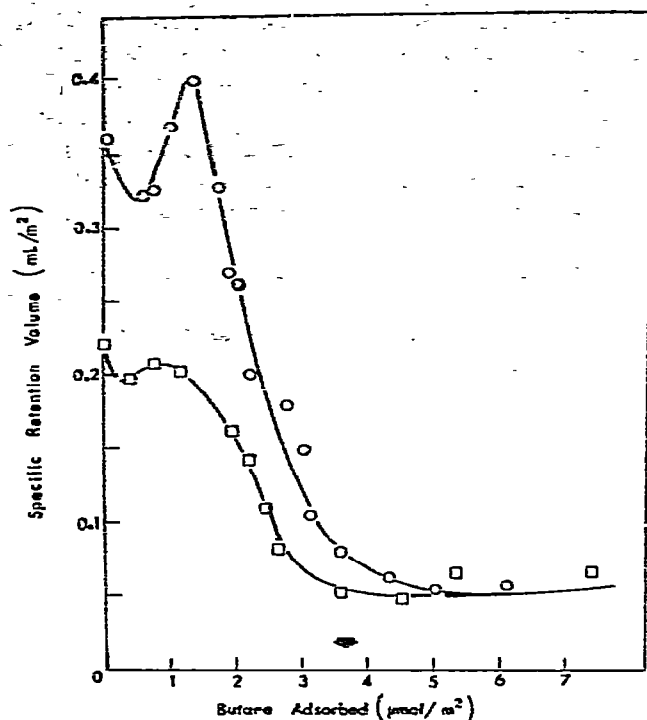
Fig. 1. Specific retention volume of propane as a function of the amount of butane adsorbed on graphitized carbon black at 10°C. O = Carbopack C; □ = Carbopack C with 0.2% Carbowax 1500.

Binary gas–solid adsorption isotherms of several systems have been measured recently by several methods including tracer pulse methods. The experimental data has been used to test and develop adsorption theories. There is, however, a paucity of experimental data for binary or more complex systems, especially for very nonideal systems. Tracer pulse methods could be used to rapidly produce a large set of experimental data to provide a sound base for further theoretical development.

Liquid adsorbates have also been used with radioactive tracers for tracer pulse chromatography[22]. Increased use of liquid chromatography–mass spectrometry will, hopefully, produce more investigations in this area. The retention mechanisms for the many different forms of high-performance liquid chromatography, especially reversed phase chromatography with an organic modifier, are not well understood, and tracer pulse chromatography could be an excellent experimental technique for the investigation of such systems.

The chromatographic applications of modified adsorbents, vapor carrier gases, and support deactivation agents, such as steam, formic acid, and ammonia, are manifold, but only partially understood and few quantitative investigations have been carried out. It has often been shown that a small amount of a sorbable vapor in the carrier gas can have a tremendous effect upon the retention times and peak shapes of the solutes in an injected sample. The effect of the vapor is determined by the amount adsorbed in the liquid or solid stationary phase. This adsorption is determined by the pressure or mole fraction of the vapor in the carrier gas. This presents the possibility of pressure or adsorption "programming" to release samples collected on an ad-

sorbent or to produce chromatographic effects similar to temperature programming while avoiding high temperatures. -

Fig. 1 also illustrates another potentially valuable application of this technique; that is the determination of surface areas for solid or liquid-modified adsorbents. The arrow in the figure shows the calculated monolayer coverage for butane on Carbopack C (12 m^2/g) assuming a coverage of 44.8 Å for butane[23]. It is obvious from the figure that the sharp decrease in the retention volume of the probe solute (propane) corresponds to the completion of a monolayer of butane on the surface. This method is similar to that proposed by Serpinet[24] for the determination of surface areas using different coatings of a nonvolatile liquid. This tracer pulse method is based on the same principle, but requires only one column. The difference between the two curves in Fig. 1 could be used to determine the surface area of the liquid CW 1500 modifier. In addition, the method does not require any isotherm model, such as the common BET equation; and it is fast, direct, and applicable to a wide variety of systems.

In summary, tracer pulse chromatography has a great number of significant potential applications. The major determent to the wide-spread use of the method is the requirement for complex specific detection systems. Hopefully, improvements in these systems, such as reduction of cost, size, and complexity, will lead to further developments in the field of tracer pulse chromatography.

6. ACKNOWLEDGEMENTS

7. SUMMARY

A review of the tracer pulse form of chromatography is presented along with discussion of the basic procedures and distinguishing features of this unique method for studying phase distribution equilibria. Typical sorbate and sorbent systems are discussed and several practical applications are presented. The basic theory of the method is reviewed; a comparison of this method with other static and chromatographic methods is given; and the review concludes with a discussion of the potential applications of the tracer pulse technique.

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