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SAMPLING AND HIGH-PERFORMANCE LIQUID CHROMATOGRAPHIC ANALYSIS OF ORGANIC COMPOUNDS IN LIQUIFIED CARBON DIOXIDE

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SUMMARY

A new technique for the sampling and analysis of solutions of organic compounds in liquified carbon dioxide is described. A high-pressure sample injection valve is incorporated in a commercial high-performance liquid chromatography instrument. Pressurization of the solution diminishes the effects of nucleate boiling and gasification within the liquid phase.

INTRODUCTION

The solvent properties of liquid carbon dioxide have attracted interest for over a century since Gore first made qualitative determinations of the solubility in the liquified gas of over 50 organic and inorganic substances¹.

Much of the subsequent literature deals with the use of liquid carbon dioxide, either singly or in combination with other solvents, in the extraction of hydrocarbon mixtures²⁻⁴. A novel application of the properties of the liquid has been the extraction of hop constituents for use in the manufacture of beer. This extract is of superior purity and stability compared with conventional solvent extraction products⁵.

The Commonwealth Industrial Gases Ltd. (Alexandria, Australia) has recently released a line of products which employ compressed carbon dioxide as a unique solvent-propellant system⁶ for the aerosol dispensation of a variety of commercially significant substances, such as insecticides. In applications such as these, where the solute may be a complex organic mixture, a convenient analytical method is required for product control.

While many studies of liquid carbon dioxide have been concerned with the determination of the solubility limits of various organic compounds^{1,3,4,7-10,13}, others have investigated the phase behaviour of partially miscible binary and ternary systems^{3,4,11,12,14}. Many of the techniques reported in this literature involve the measurement of the position of phase boundaries of mixtures contained in glass vessels, usually narrow-bore glass tubes, or liquid level gauges manufactured for service on ultra-high-pressure steam boilers. Calibration of the vessel volume was

performed by weighing in amounts of distilled water and measuring the height of the meniscus. A known amount of solute was added to the vessel, solvent carbon dioxide admitted, and the temperature of solution formation noted.

For amounts of material too small to observe the disappearance of the solute, Büchner¹² measured the elevation in critical temperature as a criterion for solubility. Elevation of the critical temperature of dilute solutions of liquid carbon dioxide, liquid sulphur dioxide, and liquid ammonia has been correlated with the mole-fraction of solute¹⁵. Quinn^{9,10} used a gravimetric technique whereby the solvent carbon dioxide was removed and the non-volatile solute weighed.

A major source of errors with these methods is the determination of the mass of carbon dioxide in solution: since carbon dioxide necessarily liquefies under high pressure, the mass of the vapour phase may be a significant fraction of the total mass. Francis² employed glass floats of various densities to estimate the liquid-phase density. Quinn used a specially designed pycnometer to measure the solution density. This method required correction for the mass of the vapour-phase carbon dioxide.

Significant volume contractions on mixing organic compounds with liquid carbon dioxide have been reported^{4,14}. Such contractions in the liquid phase will increase the equilibrium liquid-phase density relative to that of the pure solvent.

This paper describes a new analytical technique which permits the quantitative determination of the composition of solutions of organic compounds in liquified carbon dioxide. The method is based on the high operating pressures of modern liquid chromatographs.

EXPERIMENTAL

The technique involves sampling a continuous stream of solution and injecting this sample into a liquid chromatograph to effect separation of the solvent and solute components. The apparatus consists of a Valco internal-volume sample injection valve connected on-line to a Waters Assoc. high-performance liquid chromatography (HPLC) unit equipped with an ultraviolet absorption detector.

In order to examine the performance of various sampling methods, a solution of redistilled toluene in liquid carbon dioxide was used. Toluene and liquid carbon dioxide have been found to be completely miscible^{4,7}.

Procedure

A Whitey stainless-steel, double-ended sample cylinder (300 cm³ capacity) containing the solution was connected to the inlet line of the sample injection valve. A continuous stream of solution was allowed to flow through the sample valve. The flow-rate was regulated with a micrometering valve located in the sample outlet line. After passing through a series of absorption traps wherein the solute was recovered, the carbon dioxide was vented to atmosphere via a precision wet-gas meter.

Four basic sample configurations were examined for reproducibility with the internal sample valve:

- (1) Equilibrium vapour-liquid solution;
- (2) Pressurization of the vapour space to an initial value of 1000 p.s.i.g. with high purity nitrogen;
- (3) Pressurization of the vapour space to a constant value of 1000 p.s.i.g.;

(4) Hydraulically filling the sample cylinder*.

Each of the above was examined with and without the presence of a filter in the sample inlet line.

In addition, trials were conducted using standard industrial cylinders equipped with an internal tube to permit withdrawal of the liquid phase. Configuration 5 refers to the sampling of equilibrium vapour-liquid solutions of toluene in liquid CO₂ contained within these standard cylinders.

Operating conditions of the liquid chromatograph were: sample valve, Valco fixed internal volume type; sample volume, 0.2 mm³; column, Brownlee Labs RP-8 (reversed-phase type); solvent, methanol-water (90:10, v/v) flow-rate, 2.0 cm³ min⁻¹; operating pressure, *ca.* 800 p.s.i.g. at column inlet; detector, ultraviolet absorption at 254 nm (Waters Assoc. Model 440); recorder, Linear Instruments electronic integrating strip-chart recorder.

RESULTS AND DISCUSSION

Recently⁶ Commonwealth Industrial Gases Ltd. has released a range of products in Australia which uses highly compressed carbon dioxide as a solvent-propellant for the aerosol dispensation of insecticides. In large scale applications such as agricultural pest management and professional domicile treatment carbon dioxide offers both economic and environmental benefits as an alternative to conventional chlorofluoromethane systems. For quality control purposes, it is necessary to have an accurate and rapid method to identify and quantify the organic components in these systems. Because of the nature of the systems, HPLC appeared to be a convenient method for analysis.

Initially two commercial products were investigated, these being Insectigas[®] and Pestigas[®]. These products were obtained in industrial cylinders which are fabricated from aluminium and contain *ca.* 6 kg of material which is mainly carbon dioxide. Each cylinder is equipped with an internal tube fitted to the cylinder valve to permit the withdrawal of liquid phase. When cylinders of these commercial products were analysed by the procedure described under configuration 5, considerable variations in the sizes of the peaks due to the organic compounds were obtained. These variations could not be attributed to faults in the liquid chromatograph itself and so the sampling procedure was examined. Since no data on the solubilities of the active components of the insecticides in liquid CO₂ are available, one possibility was that phase separation of organics from CO₂ was occurring in the cylinder. It is known that toluene is soluble in liquid CO₂ in all proportions at temperatures above -56°C⁷. Therefore a detailed investigation of the sampling procedure was undertaken using solutions containing from 5 to 10% (w/w) in liquid CO₂ as standards.

The results of the sampling experiments are given in Table I as percentage standard deviations, calculated as the ratio of the standard deviation to the sample

* It should be noted that a cylinder which is completely filled with liquid CO₂ solution presents a potential hazard: the liquid is relatively incompressible and any increase in temperature is reflected in a large increase in pressure. Consequently, the pressure must be monitored to avoid operation near the safety limit of the vessel.

TABLE I

VARIABILITY IN TOLUENE PEAK HEIGHT FOR VARIOUS SAMPLING CONFIGURATIONS

Configuration	Variability as Percent Standard Deviation	
	With in-line filter	Without in-line filter
1	25	14
2	2	0.4
3	2.1	1.5
4	3.9	0.6
5	22	12.5

mean. The variability of toluene peak height obtained from sampling a solution of toluene in liquid CO_2 in equilibrium with its vapour is shown in Fig. 1.

Comparison of Figs. 1a and 1b illustrates the effect upon reproducibility of removal of the in-line filter. Fig. 2 shows typical data obtained from sampling a solution pressurized with nitrogen. Fig. 3 presents data obtained from experiments with hydraulically-full cylinders.

The experiments with standard industrial cylinders of Pestigas[®] and Insectigas[®] using configuration 5 yielded data of comparable variation to those obtained with configuration 1.

These results may be explained by consideration of the vapour-liquid phase diagram for carbon dioxide (Fig. 4): a cylinder containing liquid solution in equilibrium with vapour can be represented by a point such as "a" on the isotherm wxyz.

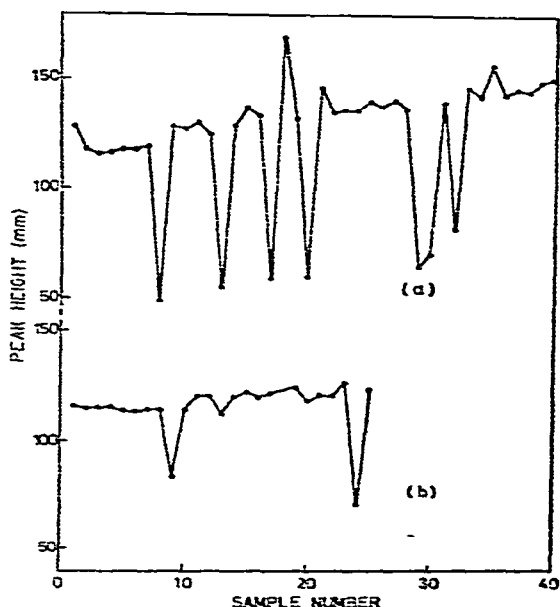


Fig. 1. Variation in peak height of toluene for configuration 1. (a) With in-line filter. (b) Without in-line filter.

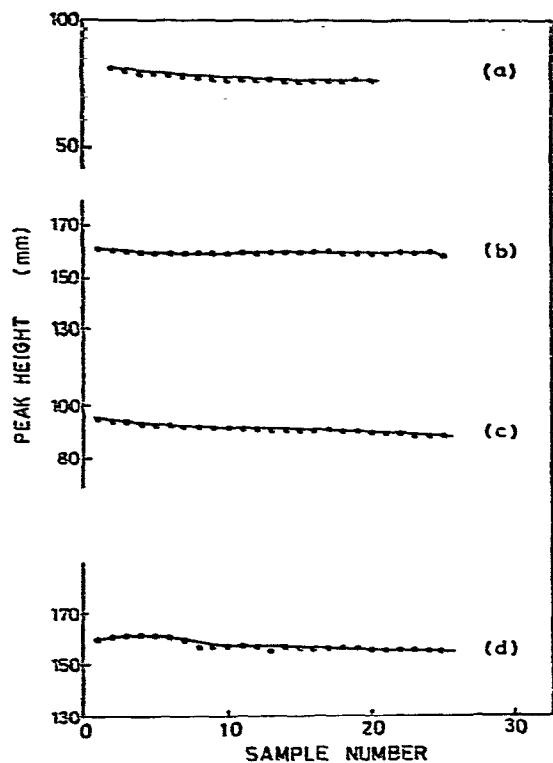


Fig. 2. Variation of peak height of toluene. (a) Configuration 2, with filter. (b) Configuration 2, without filter. (c) Configuration 3, with filter. (d) Configuration 3, without filter.

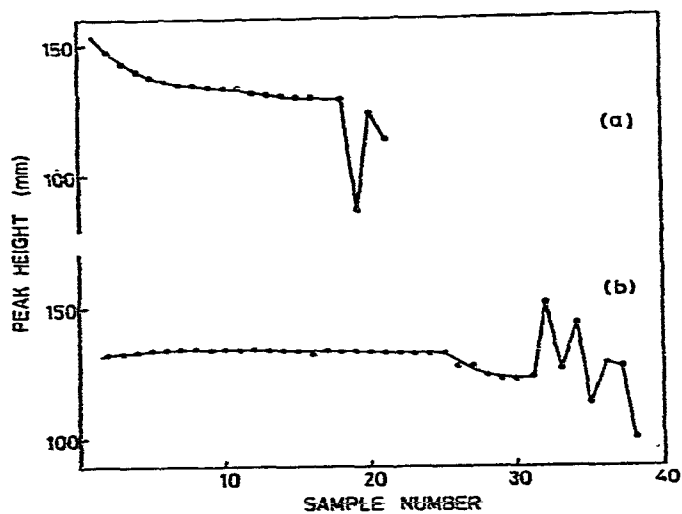


Fig. 3. Variation of peak height of toluene for configuration 4. (a) With in-line filter. (b) Without filter.

The sample stream contains no vapour and may be represented by point "y" on the co-existence curve, shown in the diagram as a dashed line. The effect on the liquid stream of volume expansions, such as caused by filters and non zero-dead-volume fittings within the sample lines, is to cause vapourization of part of the liquid stream. This process will result in the solution entering the region of two-phase equilibrium, such as at point "b".

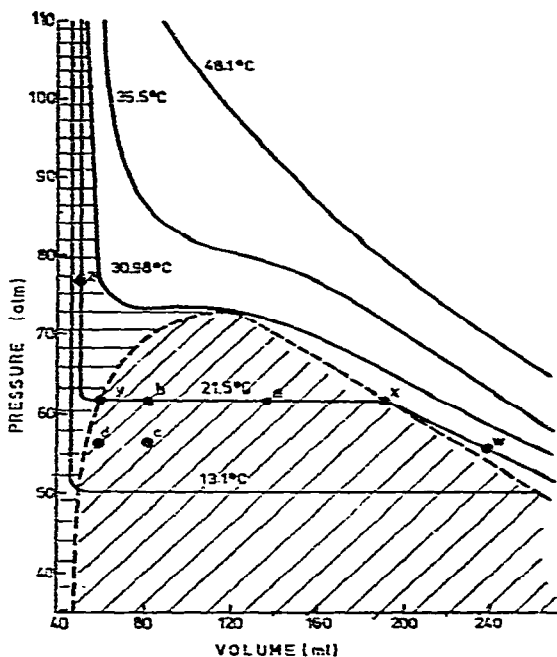


Fig. 4. Pressure-volume diagram for carbon dioxide.

Vapourization causes cooling of the fluid: the effect of vapourization and cooling is illustrated as the path "y-c". The vapour-liquid ratio at point "c" is larger than at point "b".

Under these conditions it is impossible to sample liquid only. The situation is further complicated by the fact that the solution is at its boiling point: bubble formation at macroscopic surface defects within the cylinder and sample lines means that the sample stream is non-homogeneous, a situation which gives rise to large deviations in the subsequent analysis of the samples.

The dramatic change in variability for the other configurations may be readily explained if it is postulated that the system can be represented as the point "z"; such is the case for a hydraulically-full cylinder, where the liquid phase completely fills the available volume. Small changes in the sample-line volume will not result in vapour formation. However, the liquid phase is more dense than the equilibrium value; when liquid is removed from the cylinder the density of the solution falls as the solvent expands, leading to a decrease in solution concentration. A point is reached where sufficient solution has been removed to enable vapourization within the cylinder.

An increase in variability in concentration is observed at this point and is shown in Fig. 3b.

Pressurization of the head space with nitrogen subjects the solution to a pressure greater than the equilibrium vapour pressure at that temperature, obviating nucleate boiling. This is reflected in the data.

The method outlined in this paper has been shown to be applicable to the analysis of solutions of organic compounds in liquid CO₂. In particular, it can be used to determine the nature and concentration of active constituents in commercial insecticide products propelled by liquid CO₂. The procedure is useful to determine if the active constituents have degraded and to determine if contamination has occurred in filling the cylinders. It is well known^{7,8} that liquid CO₂ is an excellent solvent for aromatic hydrocarbons. Therefore contamination of liquid CO₂ can occur from lubricating oils¹⁰ in the compression stage. The procedure described here can be used to determine if such contamination has occurred and therefore constitutes a quality control procedure for the liquified CO₂ industry.

CONCLUSIONS

A new method for the sampling and analysis of liquid carbon dioxide solutions by means of HPLC has been developed. Pressurization of the vapour space with high-purity nitrogen permits the sampling of a homogeneous liquid phase. The solute and solvent may be separated using reverse-phase liquid chromatography.

This technique may find application in the quality control programs of manufacturers of pure liquid carbon dioxide and liquid carbon dioxide-based products.

ACKNOWLEDGEMENT

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