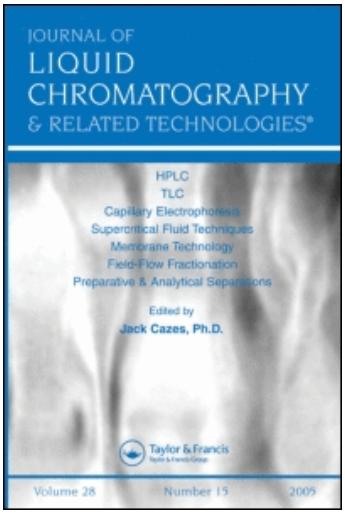

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Applications of a Technique for the HPLC Analysis of Liquid Carbon Dioxide Solutions

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APPLICATIONS OF A TECHNIQUE FOR THE HPLC ANALYSIS OF LIQUID CARBON DIOXIDE SOLUTIONS*

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ABSTRACT

A novel technique has been developed whereby substrate and solvent quantitation can be effected by means of reversed-phase high performance liquid chromatography. Carbon dioxide is detected by a differential refractometer.

Applications of this technique include the analysis of liquefied carbon dioxide-based aerosol mixtures, solubility measurements and liquid carbon dioxide extraction studies. Preliminary experiments suggest that this technique may also find application to the direct analysis of supercritical carbon dioxide extraction systems.

INTRODUCTION

Although the phenomenon of solubility of organic compounds in compressed and liquefied gases has been explored by numerous

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researchers during the past century, it is only in the last decade or so that this subject has been exploited to advantage. Some advances such as tertiary enhanced oil recovery using nitrogen and carbon dioxide miscible flooding (1,2) have fostered much basic research of vapour-liquid equilibria for selected organic-compressed gas systems (3-11). Compressed and liquefied gases have found application as extraction media and thus replaced commonly used solvents such as methylene chloride and dichloroethylene (12). Many natural products such as chrysanthemum flowers, hops, soya beans, fruit, coffee, sunflower and rapeseeds and fats and oils have yielded useful extracts when treated with liquid carbon dioxide (13-22). Other uses of liquid and supercritical carbon dioxide include the stripping of organic contaminants from activated carbon used in the treatment of wastewater (23) and the recovery of neutral oils from coal tar (24).

A patent granted in 1978 (25) demonstrated that two-phase carbon dioxide could be used to dispense as aerosols a variety of insecticides and odour absorbers, thus replacing the traditional hydrocarbon and chlorofluorocarbon solvent-propellants. As a direct result of the invention of this liquid carbon dioxide based system by the Commonwealth Industrial Gases Limited (CIG), we have been engaged in the development of suitable analytical procedures whereby condensed gas systems can be directly analyzed for their organic content. Initially aimed at facilitating the study of the physical behaviour of products based upon this technology, the developed procedures (26-28) permit the direct analysis by modern liquid chromatography of liquefied carbon dioxide solutions for quality control and fundamental solubility measurements.

The purpose of this paper is to present details of some analyses of carbon dioxide-based systems which have been performed with these procedures. Although the range of systems investigated so far is limited, it is hoped that many of the foregoing applications may benefit from the development of this novel analytical technique.

EXPERIMENTAL

Analyses were performed by means of a Waters Associates Liquid Chromatograph assembled from separate components, viz, an M6000A solvent delivery system, a model 440 absorbance detector operating at a wavelength of 254 nm and an R401 differential refractometer. Chromatograms were recorded with either a Linear Instruments dual-channel strip chart recorder or two Hewlett-Packard 3390A reporting integrators. The latter devices were modified to permit simultaneous remote start and stop and facilitated calibration and quantitation procedures.

Liquid and supercritical gas mixtures were introduced to the chromatograph by means of Valco sample injection valves of both external and internal loop configurations; various delivery volumes were used and the procedures followed for liquefied gas injection have been described elsewhere (26-28).

Separations were effected on either a Brownlee Labs RP-8 25 cm x 4.6 mm ID column or a Waters Associates μ-Bondapak C_{18} 30 cm x 3.9 mm ID column. Eluents were prepared from HPLC grade acetonitrile, freshly distilled methanol and water. All mobile phases were thoroughly degassed by vacuum filtration to 0.45 μm.

RESULTS AND DISCUSSION

Analysis of Envirosols

Envirosols is the term used in reference to the liquid carbon dioxide-based aerosol mixtures produced by CIG. There are three products in the current range: Pestigas which comprises 0.4% w/w natural pyrethrins synergized with piperonyl butoxide in liquid carbon dioxide; Insectigas, 5% w/w dichlorvos in carbon dioxide, and Deodourgas, a complex mixture of esters dissolved in liquid carbon dioxide at a concentration of 1% w/w. The most abundant components of the presently-used concentrate are triethyl citrate, isopropyl myristate and methylated resin acid

esters. This latter group of compounds comprises at least 35 components, not all of which have been identified.

Liquid samples for quality control procedures are taken directly from industrial cylinders into small volume double-ended sample cylinders and analyzed by reversed phase liquid chromatography. Sample handling is confined to pressurization with nitrogen or other inert gas (26). Figure 1 presents a chromatogram obtained from a methanolic solution of the Pestigas concentrate and one obtained from the direct injection of the liquid carbon dioxide solution. The two traces are qualitatively similar with no spurious baseline perturbations arising from the introduction of the liquefied gas. Eluted with a mobile phase comprising 85 volume percent methanol/15 volume percent water at a flowrate of 3.0 $cm^3 min^{-1}$, an analysis takes 6 minutes; temperature programmed gas chromatographic assays of the active ingredient typically require 35 minutes.

Employing the same isocratic chromatographic conditions, Insectigas is analyzed in approximately two minutes. Comparative chromatograms for this product are presented in Figure 2. The leading peak in each case is due to a product of the partial hydrolysis of the organophosphate insecticide which may occur during storage of the pure material.

The multiplicity of components in Deodourgas is illustrated in Figure 3. Although this chromatogram was obtained with elution by a 90 volume percent methanol/10 volume percent 0.01 M $(NH_4)_2HPO_4$, no significant change in the separation was observed when the buffer was omitted from the mobile phase.

The technique which permits the direct sampling and analysis of liquid carbon dioxide-based aerosol mixtures has one major advantage over other methods of quality assurance in that the need to evaporate the solvent and to then dissolve the recovered substrate in an appropriate solvent is obviated. A less apparent advantage is that solvent evaporation may result in the loss of the more volatile compounds from a complex substrate which comprises

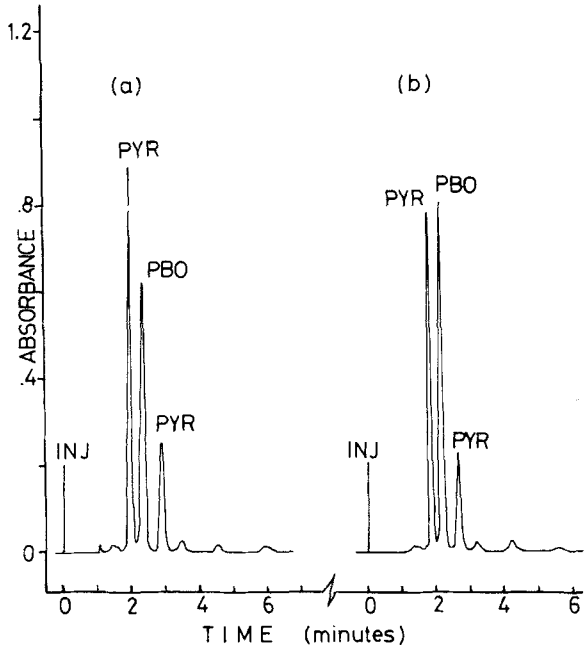

FIGURE 1. Comparative chromatograms of Pestigas Organic Solute (a) Methanolic Solution, (b) Direct CO_2 Solution Injection. HPLC conditions: sample volume - 10 mm^3; eluent - 85 v% methanol/15 v% water; flowrate - 3.0 $cm^3 min^{-1}$; column - Brownlee Labs RP8; detector sensitivity - 2.0 AUFS; chart speed - 10 mm min^{-1}.

components with widely differing boiling points. Thus direct sampling and analysis eliminates the potential loss of substrate.

Solubility Measurements

The development of a technique which would permit the determination of the limits of solubility of organic substrates in liquefied carbon dioxide (28) was an extension of the basic analytical technique (26). The technique has been tested using the naphthalene-carbon dioxide system (28) and the results obtained compare favourably with published data (29).

Although carbon dioxide does not yield a response on an ultraviolet absorbance detector, it can be detected with a differential refractometer (27). However, as illustrated in Figure 4,

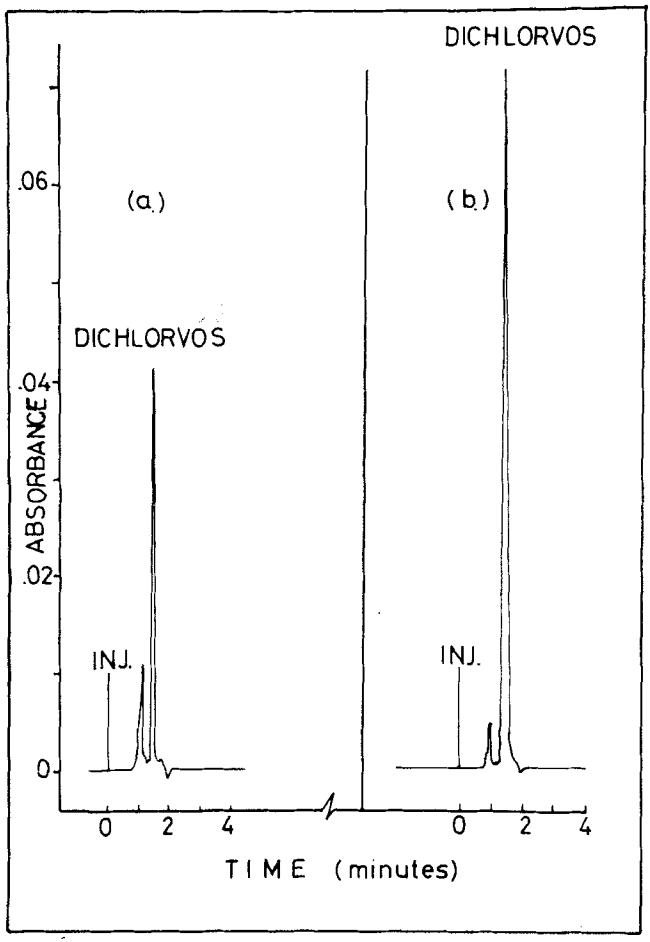

FIGURE 2. Comparative Chromatograms of Insectigas Solute (a) Methanolic Solution, (b) Direct CO_2 Solution Injection. HPLC conditions - as Figure 1 except detector sensitivity - 0.1 AUFS.

the carbon dioxide peak is of negative polarity. This arises because the refractive index of carbon dioxide is much lower than most organic compounds used as mobile phases in liquid chromatography. Consequently, the integrator must be capable of peak polarity inversion if both substrate and solvent are to be detected by means of a differential refractometer. Alternatively, two

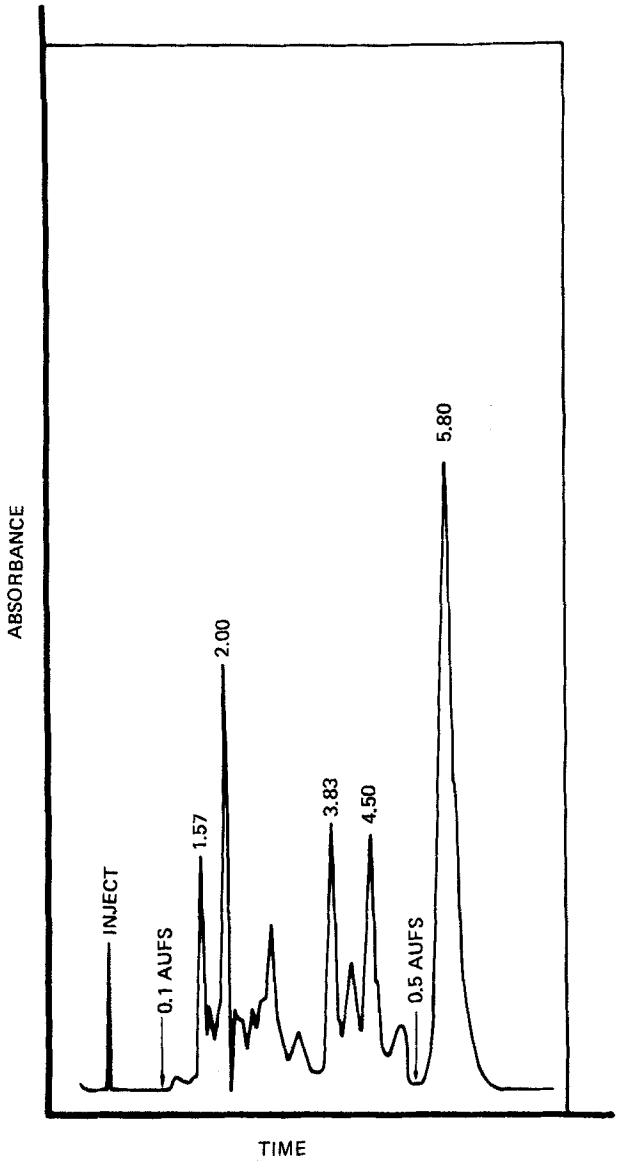

FIGURE 3. Chromatogram of Deodourgas Solute by Direct CO_2 Injection. HPLC conditions: sample volume - 10 mm^3; eluent - 90 v% methanol/10 v% 0.01 M $(NH_4)_2 HPO_4$; flowrate - 3.0 $cm^3 min^{-1}$; column - Brownlee Labs RP-8; detector sensitivity - 0.1 AUFS, 0.5 AUFS; chart speed - 10 mm min^{-1}.

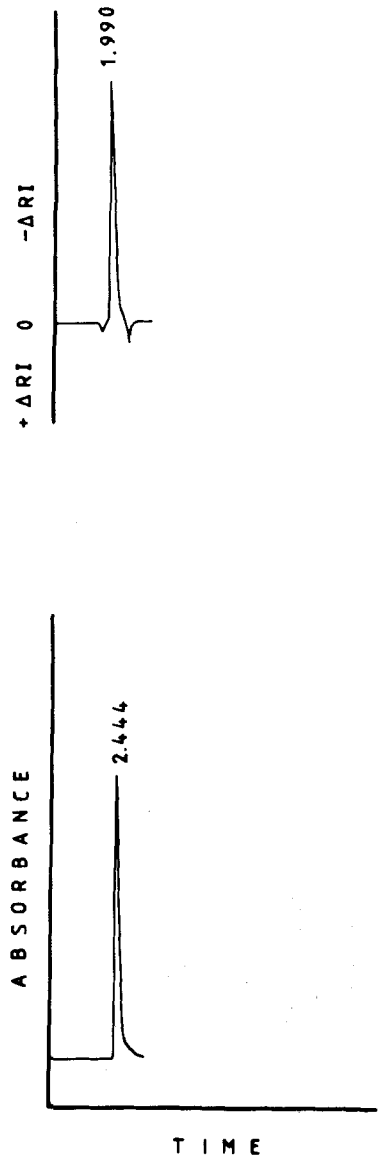

FIGURE 4. Naphthalene and Carbon Dioxide Chromatograms. HPLC conditions: sampl- volume - 2 mm^3 (nominal); eluent - 80 v% acetonitrile/20 v% water; flowrate - 2.0 $cm^3 min^{-1}$; column - Waters Associates C-18; detector sensitivity, RI-4X; UV - 2.0 AUFS; chart speed - 5 mm min^{-1}.

integrators may be interfaced to the one detector. Quantitation of carbon dioxide involves calibration of response versus absolute sample volume. It is important, therefore, that the solvent peak be separated from the solute peak if such is detected by the differential refractometer. It is fortuitous in this regard that carbon dioxide demonstrates anomalous retention behaviour in the aqueous methanol-C_{18} chromatographic system (27): the capacity factor of this compound increases very slowly with decreasing organic content in the mobile phase. Thus carbon dioxide should be readily separable from the substrate. This statement requires some qualification, however, as alkaline media are not satisfactory for carbon dioxide analyses due to reaction of CO_2 with the mobile phase (27). Alkaline substrates, such as aniline, may also cause difficulties due to adsorption on the stationary phase and the concomitant change in eluent pH in the region of the stationary phase-mobile phase boundary. In cases such as this, paired-ion chromatography in acid-buffered media may overcome this problem.

Solvent Extraction

The liquid carbon dioxide extraction from natural products of potentially useful constituents is receiving considerable attention. In order to assess the utility of the developed procedures to solvent extraction, we conducted a simple experiment involving the contacting of liquid carbon dioxide with macerated chrysanthemum cinerariaefolium flowerheads. The system was pressurized with nitrogen and the liquid analyzed by direct injection. Figure 5 illustrates both the ultraviolet absorbance and differential refractometer detector responses from an analysis of the liquid sample. A comparison of the organic substrate analysis from liquid CO_2 and commercial refined pyrethrins extract appears as Figure 6. The extract composition is similar in all respects to the commercial material with the exception of the first major peak. This component is present in the liquid carbon dioxide extract but not in the commercial product and may be a waxy compound removed in the refining process.

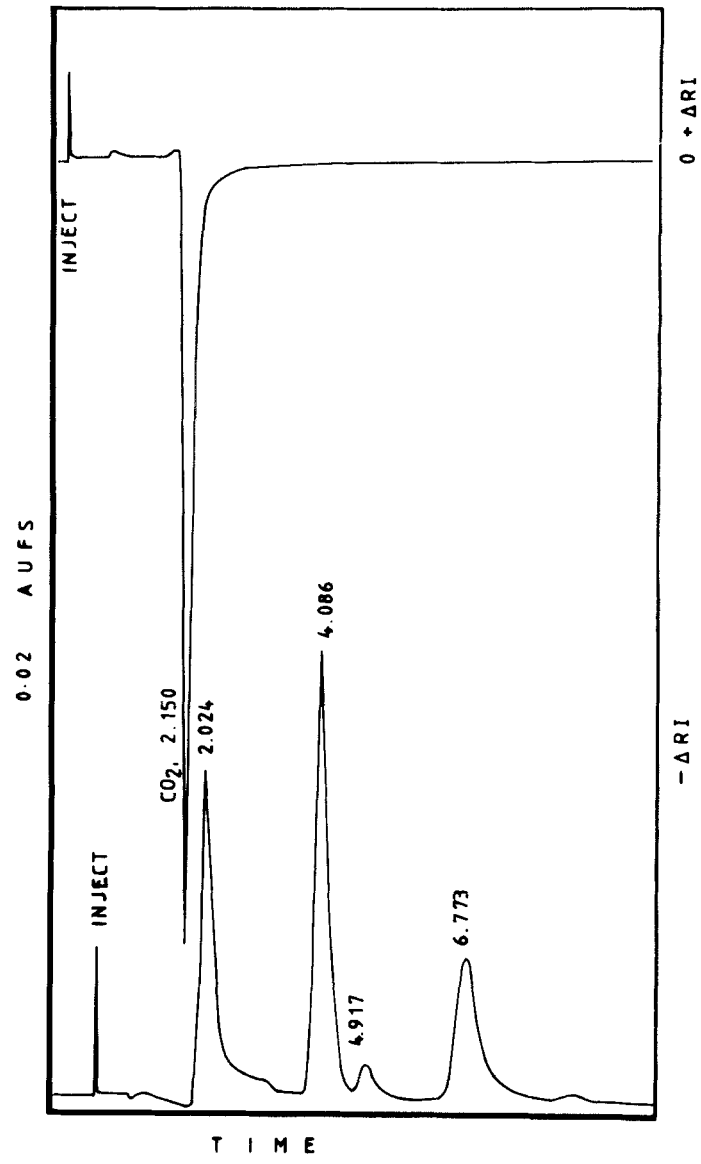

FIGURE 5. Chromatogram of CO_2-soluble Pyrethrum Extract. HPLC conditions: sample volume - 2 mm^3 (nominal); eluent 85 v% methanol/15 v% water; flowrate - 2.0 $cm^3 min^{-1}$; column - Waters Associates C-18; detector sensitivity, RI-32X; UV - 0.02 AUFS; chart speed - 10 mm min^{-1}.

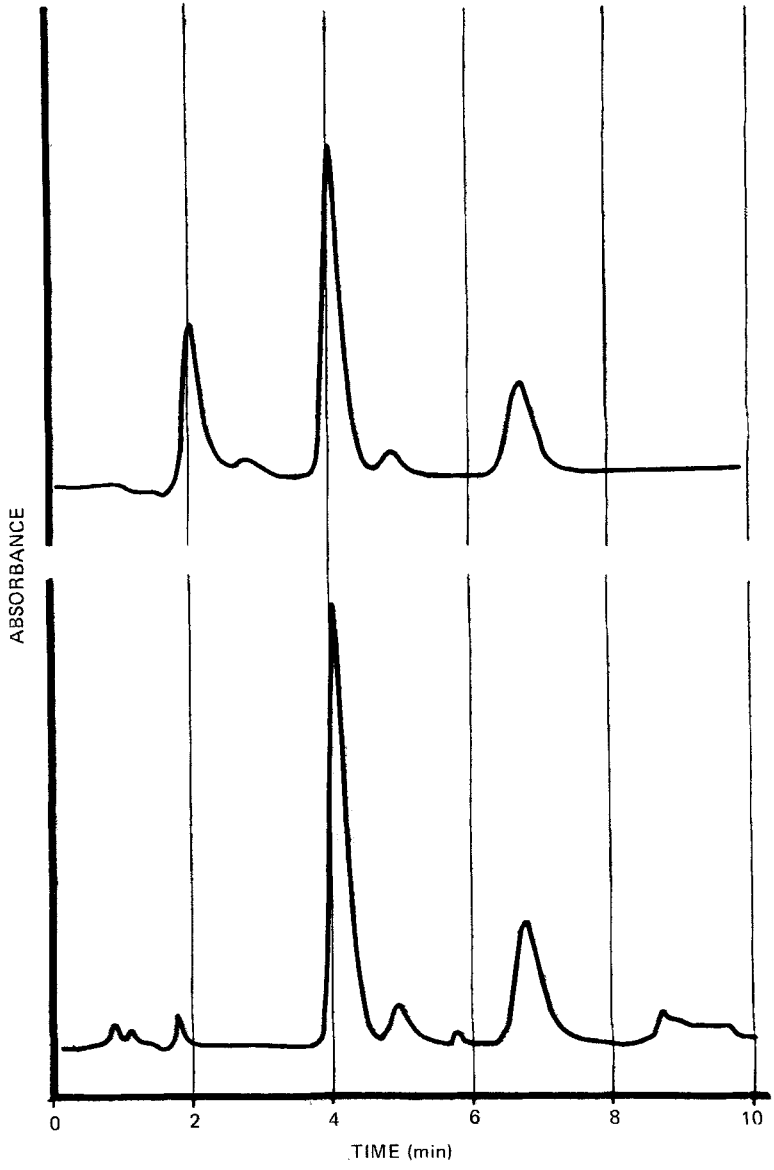

FIGURE 6. Comparison of LCO_2 and Commercial Pyrethrum Extracts. Upper - LCO_2 extract. Lower - Commercial extract. HPLC conditions - see Figure 5.

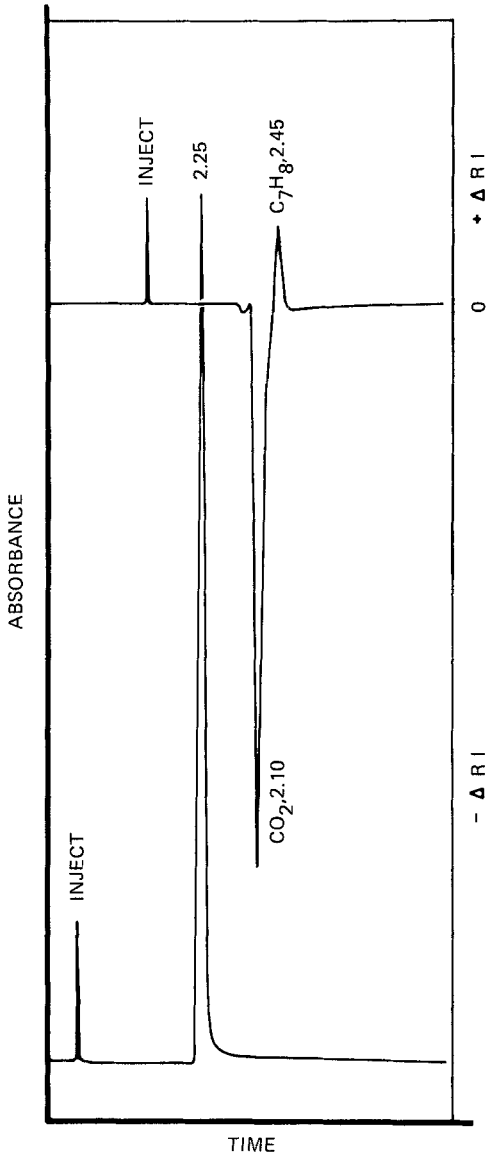

FIGURE 7. Supercritical CO_2 - Toluene Analysis. HPLC conditions: sample volume - 0.2 mm^3; eluent - 90 v% methanol/10% water; flowrate - 2.0 $cm^3 min^{-1}$; column - Waters Associates C-18; detector sensitivity, RI-32X, UV - 1.0 AUFS; chart speed - 10 mm min^{-1}.

These chromatograms indicate that carbon dioxide has a selectivity similar to that of the conventional organic solvent used in the commercial extraction of the insecticide and demonstrate that, with appropriate apparatus, the developed techniques could be of benefit to the study of liquefied gas extraction.

Supercritical Carbon Dioxide Solutions

In a previously reported study (27) it was found that liquid carbon dioxide dissolved in aqueous methanol eluents at the point of injection. It was of interest to find out whether or not supercritical carbon dioxide behaved similarly. Thus a dilute solution of toluene in liquid carbon dioxide was rendered supercritical by heating to 40°C and samples of the homogeneous fluid introduced to the chromatographic system. Sample pressure was maintained by means of a pressurized mercury reservoir (28). A chromatogram similar to that presented in Figure 7 was obtained. The carbon dioxide response is consistent with that obtained from liquid injections which demonstrates that the supercritical solution may be analyzed with reversed phase liquid chromatography.

In principle, therefore, a conventional high performance liquid chromatograph can be used for the analysis of suitable supercritical systems. Quantitative analysis relies on the availability of accurate pressure-density-temperature data for carbon dioxide.

CONCLUSIONS

We have attempted to show that a technique for the sampling and analysis of liquefied carbon dioxide solutions may be applied to activities such as quality control, solubility measurements and liquid and supercritical extraction studies. Although the technique has limitations which are primarily the suitability of the analytical method to the substrate of interest, we feel that such a technique will find many applications, not necessarily restricted to the carbon dioxide system. Indeed, the principle could be used for the analysis of many liquefied gases such as hydrocarbons.

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