

CHROM. 16,390

## Note

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### Liquid carbon dioxide as a chromatographic eluent

#### Preliminary thin-layer chromatographic experiments

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(Received October 23rd, 1983)

Carbon dioxide (CO<sub>2</sub>) exists as a subcritical liquid from -55 to +31°C within the pressure range 5-74 bar, the equilibrium pressure at 20°C being 56 bar<sup>1</sup>. Provided that liquid CO<sub>2</sub> is kept under the appropriate pressure, it can be handled like an ordinary liquid. Solubilities of many different substances in liquid CO<sub>2</sub> have been reported by Francis<sup>2</sup>, and recently several extraction procedures using liquid CO<sub>2</sub> as a solvent have been suggested<sup>3,4</sup>. These considerations prompted us to investigate the use of liquid CO<sub>2</sub> in subcritical conditions as a chromatographic eluent. As a first approach we tried to use liquid CO<sub>2</sub> as a thin-layer chromatographic (TLC) eluent. Very encouraging results have been obtained and are reported here.

#### EXPERIMENTAL

##### *Reagents*

The compounds tested were pure products from Fluka (Buchs, Switzerland). Fluorescent silica gel (60 F<sub>254</sub>) and reversed-phase (Stratocrom SI F<sub>254</sub> C<sub>18</sub> W) thin layers were obtained from Carlo Erba (Milan, Italy). Liquid CO<sub>2</sub> cylinders equipped with an eductor tube were purchased from SON (Naples, Italy).

##### *Chromatographic apparatus*

A Mahler calorimetric bomb, slightly modified, thermostated at 20°C in a water-bath, was used as the chromatographic apparatus (Fig. 1). The layer, loaded with the sample, is hung through the movable support A. Then the cover is applied on the body of the bomb and liquid CO<sub>2</sub> is introduced from a reservoir equipped with an eductor tube, by keeping open valve B for few seconds. Then valve B is closed and liquid CO<sub>2</sub> starts to fill the bomb. After about 30 sec, valve C of the reservoir is closed. The height of the liquid is ensured by letting liquid CO<sub>2</sub> flow through valve B. When the overflow of liquid CO<sub>2</sub> stops, valve B is closed. The bottom of the layer is then introduced into the liquid phase, by acting on the support D. After 10 min, CO<sub>2</sub> is allowed to evaporate by opening valve B, then the cover is removed and the layer is recovered. Spots are detected by means of iodine or UV methods.

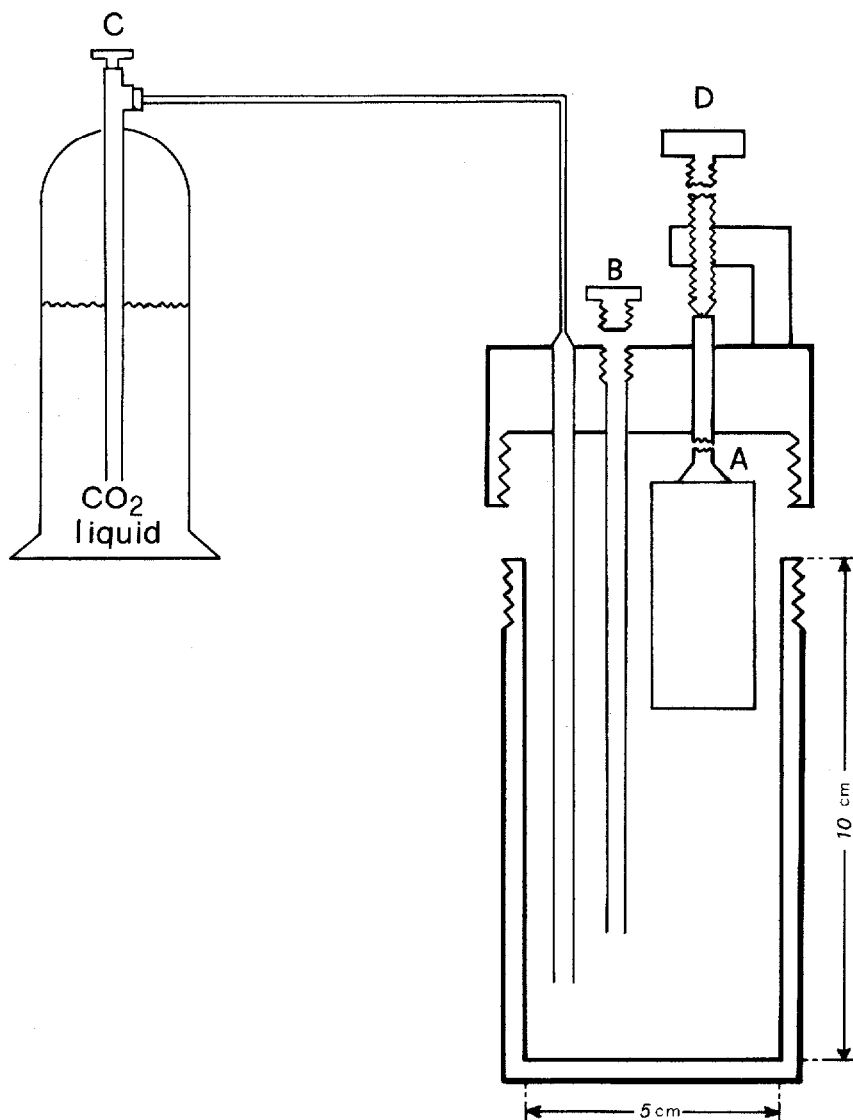


Fig. 1. Chromatographic apparatus for TLC when using liquid CO<sub>2</sub> as the eluent.

## RESULTS AND DISCUSSION

$R_F$  values of various compounds observed on silica and reversed-phase thin layers using liquid CO<sub>2</sub> are reported in Table I; as the polarity of liquid CO<sub>2</sub> is similar to that of *n*-pentane or *n*-hexane<sup>1</sup>,  $R_F$  values observed with *n*-hexane are reported. It is noteworthy that (i) liquid CO<sub>2</sub> elutes only aromatic compounds on either layer and (ii) the eluent properties of liquid CO<sub>2</sub> appear to be very different from those of a linear hydrocarbon such as *n*-hexane. Therefore liquid CO<sub>2</sub> could be used as a selective eluent for aromatic compounds and particularly for polycyclic hydrocar-

TABLE I

$R_F$  VALUES OBTAINED FOR DIFFERENT COMPOUNDS ON SILICA AND REVERSED-PHASE ( $C_{18}$ ) THIN LAYERS USING LIQUID  $CO_2$  AND  $n$ -HEXANE AS ELUENTS

Compound	$SiO_2$		Reversed phase ( $C_{18}$ )	
	Liquid $CO_2$	$n$ -Hexane	Liquid $CO_2$	$n$ -Hexane
<i>n</i> -Pentadecane	0.00	0.73	0.00	0.86
<i>n</i> -Octadecane	0.00	0.73	0.00	
1-Decanol	0.08	0.00	0.00	0.61
1-Hendecanol	0.08	0.00	0.00	
1-Dodecanol	0.08	0.00	0.00	
Lauric acid	0.00	0.27	0.00	
Myristic acid	0.00	0.27	0.00	0.91
Palmitic acid	0.00	0.27	0.00	
Methyl laurate	0.00	0.70	0.00	
Methyl myristate	0.00	0.70	0.00	0.89
Methyl palmitate	0.00	0.70	0.00	
<i>o</i> -Cresol	0.08	0.00	0.66	0.05
<i>m</i> -Cresol	0.14	0.00	0.87	0.07
<i>p</i> -Cresol	0.09	0.00	0.74	0.07
<i>o</i> -Xylene	0.07	0.00	1.00	0.21
<i>m</i> -Xylene	0.04	0.00	1.00	
<i>p</i> -Xylene	0.08	0.00	1.00	0.17
Fluorene	0.84	0.38	1.00	0.65
Anthracene	1.00		0.59	0.09
Phenanthrene	0.80	0.39	0.88	0.62
Fluoranthene	1.00	0.39	1.00	0.59
Pyrene	1.00	0.42	1.00	0.59
Methylpyrene		0.39	0.84	0.59
Benzo[ <i>a</i> ]pyrene		0.26	0.38	0.49

bons. Such a procedure could then be of some use in toxicological studies involving this class of compound.

Table II reports  $R_F$  values of non-aromatic compounds which are eluted by liquid  $CO_2$  in the presence of formic acid (100:1, v/v). The addition of a small amount of formic acid changes extensively the eluent properties of liquid  $CO_2$ . In this way, the elution of saturated compounds is possible. It is noteworthy that under such

TABLE II

$R_F$  VALUES OBTAINED FOR DIFFERENT COMPOUNDS ON SILICA GEL LAYERS USING LIQUID  $CO_2$ -FORMIC ACID (100:1) AS THE ELUENT

Compound	$R_F$ value	Compound	$R_F$ value
<i>n</i> -Pentadecane	1.00	Lauric acid	0.60
<i>n</i> -Octadecane	1.00	Myristic acid	0.45
1-Decanol	0.28	Palmitic acid	0.27
1-Hendecanol	0.20	Methyl laurate	
1-Dodecanol	0.15	Methyl myristate	0.91
		Methyl palmitate	0.78

conditions saturated hydrocarbons move to the front. Furthermore, separations on silica gel layers of homologous components (alcohols, free fatty acids, fatty acid esters) are observed; to our knowledge such a separation on silica gel layers has never been reported.

The experimental evidence reported above strongly suggests that further development of this procedure would be valuable. The apparatus described here is easily handled, the main limitation being the absence of a window to look into the bomb. The use of a visual autoclave would allow the chromatographic process to be followed directly and would make TLC with liquid CO<sub>2</sub> as simple as normal techniques.

In addition to the low cost and the safety of liquid CO<sub>2</sub>, the easy removal of the eluent should also be emphasized. In fact, liquid chromatography in general, and TLC in particular, are disadvantageous compared with gas chromatography, because of the lack of a sensitive and universal detector such as flame-ionization detector. Attempts to introduce a commercial apparatus based on such a principle in TLC, e.g. the Iatrosan TH-10 (Iatron Labs., Tokyo, Japan), in our opinion have failed so far, because of the high background level due to the organic solvents left on the layer. The use of liquid CO<sub>2</sub> or liquid CO<sub>2</sub>-formic acid, would avoid such an inconvenience.

#### ACKNOWLEDGEMENTS

We thank Professor G. Marino for his advice. This work was supported by a grant from the Ministero della Pubblica Istruzione to G.N.

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