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ION-MODERATED PARTITION CHROMATOGRAPHIC DETERMINATION OF $Ca^{14}CO_3$ AND $Ba^{14}CO_3$ SELF-RADIOLYSIS PRODUCTS

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SUMMARY

Ion-moderated partition chromatography, using strongly acidic cation-exchange resins, was used to separate five carboxylic acids (formic, oxalic, glyoxylic, glycolic and acetic) and seven one- and two-carbon non-ionic compounds (methanol, ethanol, ethylene glycol, formaldehyde, glyoxal, acetaldehyde and methyl formate). The carboxylic acids could not be separated from their corresponding aldehydes. Quantification of the compounds was achieved by using a combined analysis: in the first run, the mixtures were separated using only the cation-exchange column; before the second run, a short anion-exchange column was inserted between the cation-exchange column and the detector to remove the acids, collecting only the non-ionic compounds. This method was used to identify and quantify the organic products formed in the self-radiolysis of solid $Ca^{14}CO_3$ and $Ba^{14}CO_3$. All five acids, formaldehyde and methanol were found.

INTRODUCTION

A large number of chromatographic techniques have been used for the separation of carboxylic acids[1,2]. Of these, the most successful appears to be ion-exclusion partition chromatography[3–7], perhaps better called ion-moderated partition chromatography[8]. This process, which uses a strongly acidic cation-exchange resin as the stationary phase with aqueous mobile phases at high[7–9] or medium pressures[3,4,10,11], also separates non-ionic compounds[12]. Recently, a strong cation exchanger was used to separate several homologous series of non-ionic compounds (aldehydes, ketones or alcohols), and also a mixture of some of these compounds[13].

This paper reports the separation of several non-homologous compounds containing one or two carbon atoms by ion-moderated partition chromatography and the application of this procedure to the identification and quantification of the products resulting from the self-radiolysis of ^{14}C-labelled carbonates.

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EXPERIMENTAL

Chromatographic systems

The high-pressure system consisted of an Altex Model 110 A reciprocating pump, a Rheodyne Model 7010 injection valve, a stainless-steel column (25 × 0.46 cm I.D.) and a Schoeffel Spectroflow Model 770 detector (Kratos Analytical) used with an 8-μl cell at 210 nm. The medium-pressure system consisted of a Milton-Roy minipump, a septum injector, a water-jacketed glass column (100 × 0.55 cm I.D.) and a Varian Aerograph Series 512 refractive index detector used at maximum sensitivity. The column and detector were maintained at the same temperature (37°C) with a circulating water-bath (Varian Aerograph Model 4100). Fractions were collected using an ISCO Model 328 collector.

Stationary phases

The Bio-Rad strong cation-exchange resins Aminex A-5 (13 μm) and AG 50W-X12 (<37 μm) were used in the H^+ form. Before packing, the resins were washed successively with 0.2 *M* sodium hydroxide solution, 2 *M* sodium hydroxide solution, deionized water, 0.1 *M* hydrochloric acid, 1.0 *M* hydrochloric acid and water (to neutral pH). For some separations, a short polyethylene column (10 × 0.2 cm I.D.), containing Bio-Rad AG 1-X8 anion-exchange resin (<37 μm) in the OH^- form, was added to the system. All columns were packed in our laboratory using, when necessary, a Shandon HPLC packing system.

Mobile phases

The eluents were deionized water and dilute solutions of perchloric or sulphuric acid.

Compounds

Barium carbonate labelled with ^{14}C (10.7 GBq/g) was obtained from New England Nuclear. ^{14}C-labelled calcium carbonate was prepared from $Ba^{14}CO_3$ by a modification of the procedure of Pfeiffer *et al.*[14]. Solutions of formic, oxalic, glyoxylic, glycolic and acetic acid and of methanol, ethanol, ethylene glycol, formaldehyde, glyoxal, acetaldehyde and methyl formate, all previously purified[15], were prepared at several concentrations using deionized water. The identities of most of the chromatographic peaks were confirmed with ^3H- or ^{14}C-labelled compounds (New England Nuclear).

Sample dissolution

Samples of 1 mg of $Ca^{14}CO_3$ or $Ba^{14}CO_3$ were dissolved in 100 μl of a carrier solution containing *ca.* 0.01 *M* of each of the twelve compounds listed above. The dissolution was carried out in the presence of 5 mg of cation-exchange resin (Bio-Rad AG 50W-X8, <37 μm, H^+ form) which provided the acid for the dissolution and removed the metal cation[16].

Determination of the ^{14}C-labelled compounds

The ^{14}C-labelled products were identified and quantified by a paired combined sequence using $5 \cdot 10^{-4}$ *M* sulphuric acid as the mobile phase. For the first run, a

30-μl aliquot of the dissolution solution was separated using only the cation-exchange column. Before the second run, the short anion-exchange column was connected between the cation-exchange column and the detector. In both runs, fractions were collected corresponding to the carrier peaks observed on the recorder. The ^{14}C contents of the peaks collected from both runs were then determined by liquid scintillation counting using an appropriate scintillation solvent[17].

RESULTS

Aliquots (30 μl) of the solutions of the five acids and the seven non-ionic compounds were injected singly or in mixtures to determine retention times and peak resolutions, under a variety of conditions, using both chromatographic systems. The retention times of the acids are sensitive to the pH of the eluent in the range 1.3–5.3 (Table I), as reported previously[5,7,10], but the retention times of the non-ionic compounds do not vary with pH[13]. No changes in retention times were observed at column temperatures between 5 and 50°C with mobile phases of pH 3 or higher. At pH 1.3, slight increases in the retention times of the more retained acids were observed.

Table II summarizes the best results obtained with the two different chromatographic systems. Fig. 1 shows a typical chromatogram of a mixture of the twelve compounds with the medium-pressure system. The high-pressure system provides similar separations with shorter retention times. The number of theoretical plates per metre observed for the Aminex A-5 column (high-pressure system) was 23 400, whereas for the AG 50W-X12 column (medium-pressure system) it was 4540, reflecting the effect of the particle size of the stationary phase on peak broadening.

All five carboxylic acids are separated with resolutions of 1.1 or better with either system. However, none of the elution conditions tested gave resolutions greater than 0.3 for the pairs formaldehyde–methyl formate and acetaldehyde–ethylene glycol. In addition, the aldehyde–acid pairs glyoxal–glycolic acid, formaldehyde–formic acid and acetaldehyde–acetic acid could not be resolved sufficiently to permit identification and quantification of the ^{14}C content of these compounds from fractions collected during a single analytical run. A chromatogram consisting of only the non-

TABLE I

EFFECT OF DIFFERENT MOBILE PHASE ACID CONCENTRATIONS ON THE RETENTION TIMES OF CARBOXYLIC ACIDS USING AN AMINEX A-5 COLUMN (25 × 0.46 cm I.D.) AT A FLOW-RATE OF 0.25 ml/min, WITH THE HIGH-PRESSURE SYSTEM

Carboxylic acid	*Retention times (min) at sulphuric acid concentrations*			
	$5 \cdot 10^{-6}$ *M (pH 5.3)*	$5 \cdot 10^{-4}$ *M (pH 3.3)*	$5 \cdot 10^{-3}$ *M (pH 2.3)*	$5 \cdot 10^{-2}$ *M (pH 1.3)*
Oxalic	6.0	6.6	8.0	12.0
Glyoxylic	7.6	11.2	12.4	14.0
Glycolic	12.8	16.0	17.2	19.2
Formic	14.4	18.4	20.0	22.0
Acetic	18.8	21.6	22.8	24.4

TABLE II

RETENTION TIMES FOR FIVE CARBOXYLIC ACIDS AND SEVEN NON-IONIC COMPOUNDS WITH $5 \cdot 10^{-4}$ *M* H_2SO_4 AS MOBILE PHASE

Carboxylic acid	*Retention time (min)*			*Non-ionic compound*	*Retention time (min)*		
	Aminex A-5 (HPLC)*	*AG 50W-X12 (HPLC*)*	*AG 50W-X12 (MPLC**)*		*Aminex A-5 (HPLC*)*	*AG 50W-X12 (HPLC*)*	*AG 50W-X12 (MPLC**)*
Oxalic	6.5	7.5	26.1	Glyoxal	9.0	9.0	29.1
Glyoxylic	9.0	9.0	28.9	Formaldehyde	12.0	12.0	36.5
Glycolic	11.5	10.5	34.2	Methyl formate	13.0	12.5	37.1
Formic	13.5	12.0	38.2	Acetaldehyde	14.5	14.0	41.5
Acetic	15.0	14.5	41.8	Ethylene glycol	15.0	15.0	42.5
				Methanol	17.0	17.0	51.7
				Ethanol	18.5	19.0	60.1

* HPLC = high-pressure liquid chromatography; flow-rate, 0.20 ml/min.
** MPLC = medium-pressure liquid chromatography; flow-rate, 0.36 ml/min.

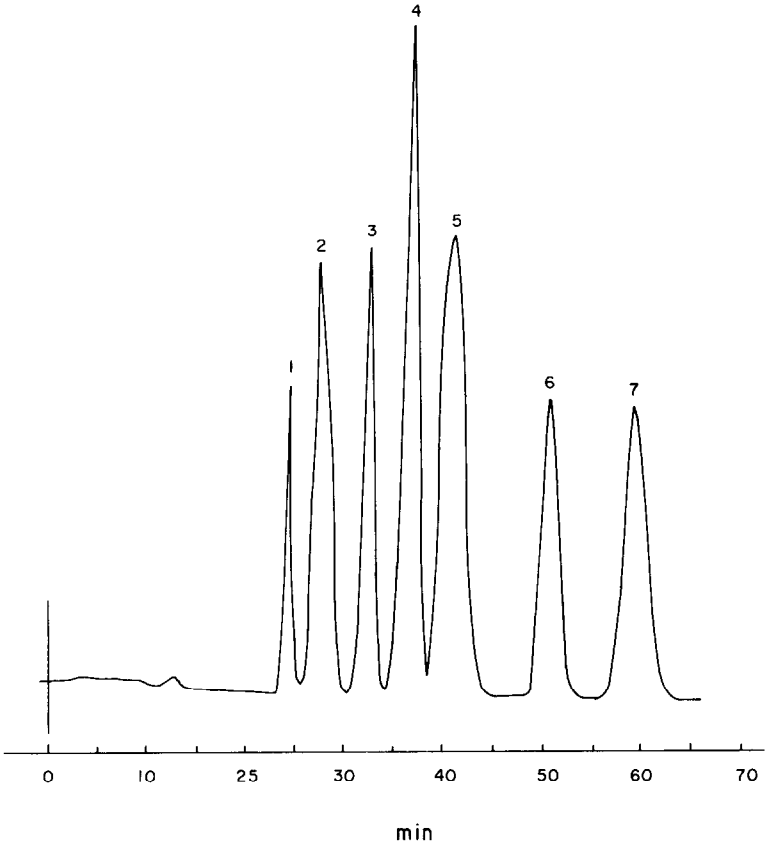

Fig. 1. Ion-moderated partition chromatographic separation of a mixture of five carboxylic acids and seven non-ionic compounds using a Bio-Rad AG 50W-X12 (100 × 0.55 cm I.D.) column with $5 \cdot 10^{-4}$ *M* sulphuric acid at 0.36 ml/min in the medium-pressure system with refractive index detection. Peaks: 1 = oxalic acid; 2 = glyoxal + glyoxylic acid; 3 = glycolic acid; 4 = formaldehyde + formic acid + methyl formate; 5 = acetaldehyde + acetic acid + ethylene glycol; 6 = methanol; 7 = ethanol.

ionic compounds was obtained when a short anion-exchange column was added to the system to retain the carboxylic acids, without changing the separation of the non-ionic compounds (Fig. 2).

Collection of peaks relating to the chromatograms obtained with and without the anion-exchange column permitted the identification and quantification of the self-radiolysis products from solid $Ca^{14}CO_3$ and $Ba^{14}CO_3$. As indicated in Table III, within the detection limits of this method, $Ba^{14}CO_3$ self-radiolysis products include formic, oxalic, glyoxylic, glycolic and acetic acids and formaldehyde. The same products, plus methanol, are seen from $Ca^{14}CO_3$, although in different amounts. No non-ionic products containing two carbon atoms were detected.

Our results indicate the effectiveness of ion-moderated partition chromatography using a cation-exchange resin as a separation technique which applies several different interaction processes (ion exclusion, size exclusion and normal- and re-

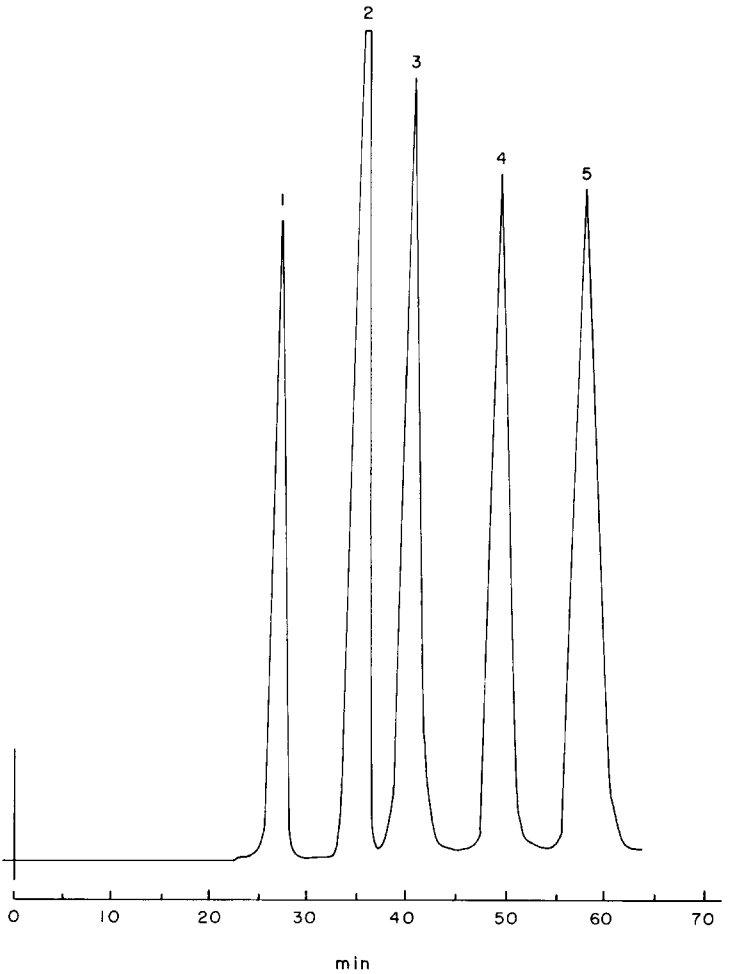

Fig. 2. Separation of a mixture of five carboxylic acids and seven non-ionic compounds using a Bio-Rad AG 50W-X12 column (100 × 0.55 cm I.D.) and a Bio-Rad AG 1-X8 (OH^-) column (10 × 0.2 cm I.D.) in series. All other conditions as in Fig. 1. Peaks: 1 = glyoxal; 2 = formaldehyde + methyl formate; 3 = acetaldehyde + ethylene glycol; 4 = methanol; 5 = ethanol.

TABLE III

SELF-RADIOLYSIS PRODUCTS (%) FROM HEAVILY IRRADIATED $Ca^{14}CO_3$ AND $Ba^{14}CO_3$

Product	$Ca^{14}CO_3$	$Ba^{14}CO_3$
Formic acid	80.7	57.5
Oxalic acid	12.2	9 1
Glyoxylic acid	3.2	10.4
Glycolic acid	0 6	2.0
Acetic acid	2.3	20.5
Formaldehyde	0.8	0.5
Methanol	0.2	Nd*

* Nd = Not detected.

versed-phase partition) simultaneously to resolve a non-homologous mixture. We can also confirm that for these purposes both the high- and medium-pressure separations proved effective, the high-pressure procedure having the advantage of shorter separation times.

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