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MACROPOROUS CATION EXCHANGERS IN GAS CHROMATOGRAPHY

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SUMMARY

Macroporous sulphate-bonded cation exchangers based on copolymers of styrene and divinylbenzene were used in gas chromatography for the separation of compounds with similar physicochemical properties, the identification of non-polar or weakly polar organic admixtures in solvents and sewage, the separation of alkanes, alkenes, aromatic and chlorinated hydrocarbons as well as for the analysis of gas mixtures for environmental purpose.

INTRODUCTION

Macroporous ion-exchange resins are of great interest for gas chromatography (GC) due to their being highly selective polymeric sorbents¹⁻³. The local positive charge on the hydrogen and metal ions of their ionogenic groups as well as the electronic structure of the cations bound to the porous polymeric matrix result in highly specific donor-acceptor interactions with sorbates, including hydrogen bonding and π -complex formation. Such interactions can be utilized in GC to affect the elution order and accomplish previously impracticable separations.

EXPERIMENTAL

Analyses were carried out using Tsvet 132 and LKhM 8md chromatographs equipped with thermal conductivity detectors, on 0.4-2.5 m \times 3 mm I.D. columns at 20-200°C and using helium as carrier gas at a flow-rate of 30-80 ml/min.

RESULTS AND DISCUSSION

Table I presents relative retention times for some compounds on a macroporous sulphate-bonded cation exchanger KU 23 (H^+ and Co^{2+}) and one based on Polysorb (Ni^{2+} , Cu^{2+} , K^+ , Ca^{2+} and Zn^{2+}). The separation factors are substantially higher than those obtained with such sorbents as Porapak and Chromosorb, which indicates the high selectivity of macroporous cation exchangers and permits their application to the GC separation of compounds of various classes.

The cobalt(II) form of the KU 23 cation exchanger shows irreversible retention of ammonia and amines, very strong retention of nitriles, alcohols, water and organic

TABLE I
RELATIVE RETENTION TIMES FOR CERTAIN COMPOUNDS ON MACROPOROUS SULPHATE-BONDED CATION EXCHANGERS AT 150°C

Sorbate	Retention time relative to <i>n</i> -pentane						
	KU-23 (H ⁺)	Sulphate-bonded Polysorb					
		Co ²⁺	K ⁺	Ca ²⁺	Ni ²⁺	Cu ²⁺	Zn ²⁺
Water	51.3	538.4	417.0	430.5	552.3	348.5	823.0
Methanol	—	489.5	242.0	279.3	405.7	178.5	735.0
Acetone	66.3	19.9	257.0	134.3	31.7	9.5	170.5
Acetonitrile	26.0	258.4	277.0	219.3	199.0	248.5	270.0
Diethyl ether	20.7	5.0	9.0	9.8	13.7	7.9	9.5
Methylene chloride	6.9	10.4	64.0	19.3	19.7	22.5	24.0
Chloroform	11.0	3.3	11.0	2.7	2.3	3.0	4.0
Carbon tetrachloride	1.5	2.3	3.0	1.3	1.5	2.4	3.0
Cyclohexane	1.3	1.7	5.0	1.5	1.6	1.7	1.5
Cyclohexane	2.0	1.9	8.0	2.3	2.4	30.6	2.5
Benzene	15.0	3.0	10.0	5.4	3.3	6.4	4.5
Toluene	20.7	5.1	16.0	5.9	5.9	14.0	7.0

acids and fairly strong retention of ketones, ethers and nitro compounds as compared to alkanes³. The high selectivity of sulphate-bonded cation exchangers allows their use as subtracting agents in the subtraction method.

On the hydrogen form of the cation exchanger the elution order and retention data are substantially different from those on Co²⁺, Zn²⁺, Ni²⁺, K⁺, Ca²⁺ and Cu²⁺, indicating different types of sorbate-cation exchanger interactions in the two cases. Thus, on the hydrogen form, chloromethane derivatives are eluted in the order tetrachloro, dichloro, monochloro, *i.e.*, in accord with their ability to participate in hydrogen bonding to the cation-exchanger protons, while on the other forms the elution order is determined by complex formation in the coordination sphere of a metal counter ion (Table I). On sulphate-bonded cation exchangers the order of elution of chloromethane derivatives is different from that observed on conventional polymeric sorbents and liquid stationary phases, which makes easier the identification of compounds and the analysis of organic components in aqueous and organic media.

Macroporous sulphate-bonded cation exchangers are peculiar in showing weak retention of alkanes, retention times for C₁-C₁₀ compounds being as short as 3-5 min. This makes it worthwhile to use these sorbents in the analysis of petrol, exhaust gases and hydrocarbons present in sewage and polar organic solvents (Fig. 1), as well as in the group separation of hydrocarbons and polar organic compounds.

Also promising is the use of the above sorbents in the separation of alkanes, alkenes and aromatic hydrocarbons, whose determination is important in the GC of oil products. To characterize the selectivities of the sorbents, Table I presents the separation factors for these compounds on the various forms of the cation exchangers. The forms H⁺, Co²⁺ and K⁺ are seen to be highly selective for aromatic compounds and the copper(II) form for alkanes (Tables I and II), which, in particular, results in the elution of cyclohexene after benzene and toluene, with good resolution

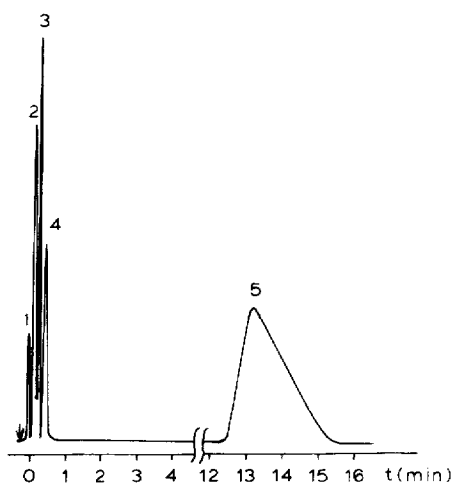


Fig. 1. Chromatogram of C_1 - C_{10} hydrocarbons in water. Sorbent: sulphate-bonded cation exchanger in the zinc form. Column: $0.65 \text{ m} \times 3 \text{ mm}$ I.D. Temperature: 150°C . Helium carrier gas flow-rate: 30 ml/min .

(Fig. 2). The high selectivity of the copper(II) form is due to the ability of Cu^{2+} to form tight π -complexes through donor-acceptor interactions with alkenes and less tight ones with aromatic hydrocarbons, which results in the elution of compounds with equal numbers of carbon atoms in the order alkanes, aromatic hydrocarbons, alkenes. In its ability selectively to adsorb alkenes, this form of the sulphate-bonded cation exchanger is similar to stationary liquid phases containing silver or rhodium salts, but it excels them in selectivity and thermal stability. According to thermogravimetric evidence, the sorbents in the copper(II) form are stable up to 200°C , compared to 65°C for the stationary liquid phase containing silver nitrate in ethylene glycol, and can be used for the separation of C_2 - C_{12} hydrocarbons.

TABLE II

SELECTIVITY FACTORS, k , FOR SEPARATION OF MIXTURES ON DIFFERENT SORBENTS

$k = t'_R$ for alkenes/ t'_R for aromatic hydrocarbons.

Sorbates	Selectivity factors at 150°C		
	SO_3H^- form	Ag^+ form	Cu^{2+} form
Cyclohexene/benzene	0.12	2.71	4.76
Hexene/benzene	0.24	2.51	5.00
Cyclohexene/toluene	0.05	0.86	2.18
Hexene/toluene	0.09	0.79	2.30
Cyclohexene/ethylbenzene	0.04	0.35	0.98
Hexene/ethylbenzene	0.09	0.32	1.03
Cyclohexene/ <i>o</i> -xylene	0.04	0.23	0.84
Hexene/ <i>o</i> -xylene	0.08	0.21	0.88
Cyclohexene/mesitylene	0.03	0.14	0.60
Heptene/toluene	0.06	—	3.71
Octene/ethylbenzene	0.06	—	2.80
Hexene/mesitylene	0.07	0.13	0.63

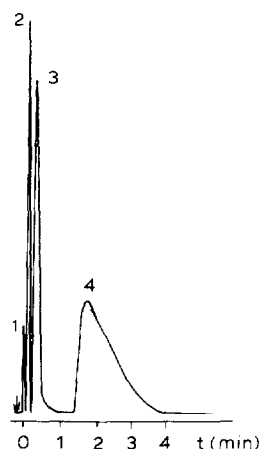


Fig. 2. Chromatogram of a mixture of air (1), cyclohexane (2), benzene (3) and cyclohexene (4). Sorbent: sulphate-bonded cation exchanger in the copper form. Column: 0.40 m \times 3 mm I.D. Other details as in Fig. 1.

Table II compares selectivity factors obtained with the copper and hydrogen forms of the polymeric sorbent Polysorb 1 and with a macroporous ion-exchange resin, Amberlyst 15 in the silver form¹. The data show that the selectivity in separating the system alkenes–aromatic hydrocarbons of the copper form is 2–4 times greater than that of the silver form and 20 times that of the hydrogen form of the cation exchanger, which permits the separation of the above hydrocarbons on columns as short as 60 cm.

The copper form of the sulphate-bonded cation exchanger does not undergo reduction on exposure to light, contrary to the silver form. This allows the use of glass columns along with metal ones. The copper form also has the advantage that copper salts are less expensive than silver ones.

The copper form of the cation exchanger also has a fairly high selectivity in separating alkenes with different structures and different locations of the double bonds (Table III). Branched alkenes and those containing substituents at the double bond show smaller retention volumes and thus form less tight complexes with Cu^{2+} compared to linear molecules.

TABLE III

RELATIVE RETENTION TIMES FOR ALKENES WITH DIFFERENT STRUCTURES AND DIFFERENT LOCATIONS OF THE DOUBLE BOND

$T = 150^\circ\text{C}$, flow-rate 60 ml/min.

Sorbate	Boiling point ($^\circ\text{C}$)	M_r	Retention time relative to <i>n</i> -hexane
1-Heptene	93.6	98.18	22.5
3-Heptene	95.8	98.18	20.8
2-Methyl-2-hexene	95.4	98.18	15.5
1-Hexene	63.5	84.16	13.6
2,3-Dimethyl-2-butene	73.2	84.16	6.9

By providing elution in the order alkanes, aromatic hydrocarbons, alkenes, macroporous sulphate-bound cation exchangers in the copper form permit the determination of alkane and aromatic hydrocarbons in the presence of alkenes. This is of great importance for purity control of alkenes used as a raw material in a number of industries, and for analysis of exhaust gases and sewage.

It should also be noted that the large retention times of alkenes allow the use of the macroporous sulphate-bonded cation exchanger (Cu^{2+}) for concentrating minor amounts of alkenes from air, exhaust gases, aromatic hydrocarbons and alkanes, as well as for the preparative isolation of alkenes by GC.

Also very promising is the use of the macroporous cation exchangers in GC of gases, since the high selectivity of these sorbents due to their ability to participate in donor-acceptor interactions results in elution orders different from those observed on other polymeric and mineral sorbents. This can be illustrated by the separation of mixtures of air and nitrogen oxides. The latter are highly reactive atmospheric pollutants. At the same time, NO is a raw material for organic synthesis, such as that of hydroxylamine used in the manufacture of copralactam. Thus, it is of importance to monitor the purity of NO. This may be accomplished when more readily impurities such as NO_2 , CO_2 and light hydrocarbons are eluted before the main component, NO.

Elution in the required order, *i.e.*, air, C_1 - C_6 hydrocarbons, NO_2 , NO, when separating a mixture of these gases can also be achieved on the copper form of the macroporous sulphate-bonded cation exchanger based on the copolymers of styrene and divinylbenzene. Strong donor-acceptor interaction between NO and Cu^{2+} results in elution of the former after NO_2 , CO_2 , H_2S and C_1 - C_6 hydrocarbons. This allows one to determine these gases when present as impurities in NO, as well as to

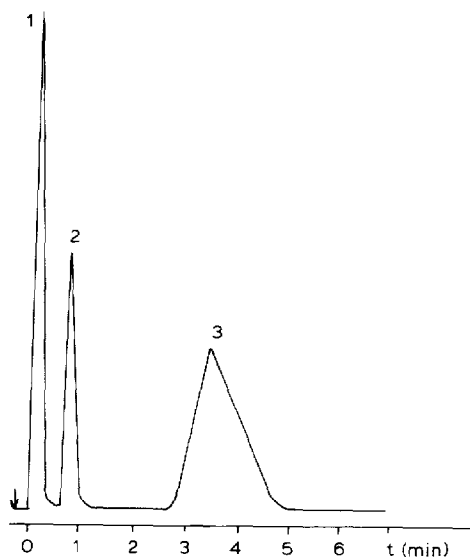


Fig. 3. Chromatogram of a gas mixture containing air (1), NO_2 (2) and NO (3). Sorbent: sulphate-bonded cation exchanger in the copper form. Column: $0.65 \text{ m} \times 3 \text{ mm}$ I.D. Temperature: 50°C . Helium carrier gas flow-rate: 30 ml/min .

analyse hydrocarbon- and nitric oxide-containing systems, such as exhaust gases. Thus, the threshold sensitivity in determining NO in flue gas using a thermal conductivity detector and helium as carrier gas is 0.02%.

Chromatograms of gas mixtures containing nitrogen oxides are shown in Figs. 3 and 4. The separation was performed on a LKhM 8md gas chromatograph with a thermal conductivity detector, a 0.6 m \times 3 mm I.D. column at 50–80°C and a helium flow-rate of 30 ml/min. The order of elution on this cation exchanger was not observed with other sorbents and stationary liquid phases, thus indicating complex formation between the copper form of the cation exchanger and NO in the course of separation. The selectivity of separation of the NO–air systems is 7–9 times and that of the NO–NO₂ ones 8–13 times greater than that on Porapak Q and on charcoal SKT with 10% nickel(II) sulphate. Table IV presents the separation factors, k , for the above systems.

Rapid elution of NO₂ from the copper form of the cation exchanger and the long retention time of NO allow these sorbents to be used for rapid determination of NO₂ in gases, in particular, in the presence of high nitric oxide concentrations.

Selective retention of NO results in large retention volumes for the gas. Thus, the specific retention volume, V_g , for NO at 18°C and a helium flow-rate of 30 ml/min is 320 ml/g. This makes it possible to use this cation exchanger as a sorbent for concentrating NO from air, CO₂, exhaust and other gases in order to accumulate sufficient amounts for its determination by GC or other means, as well as for air purification from NO. The use of the sulphate-bonded cation exchanger in the copper form for concentrating NO from, for instance, flue gases followed by thermodesorp-

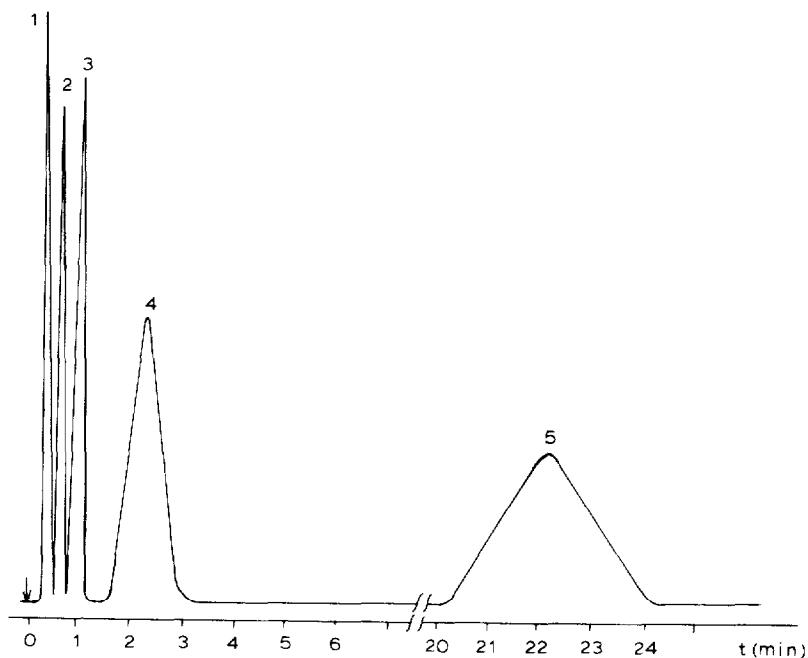


Fig. 4. Chromatogram of a gas mixture containing methane (1), hydrogen sulphide (2), hexane (3), nitric oxide (4) and water vapour (5). Sorbent and column as in Fig. 3. Temperature: 80°C. Helium carrier gas flow-rate: 40 ml/min.

TABLE IV

SEPARATION FACTORS FOR AIR AND NITROGEN OXIDES ON DIFFERENT SORBENTS

$k = t_{R1}/t_{R2}$, where t_{R1} and t_{R2} are retention times for the components compared. $T = 80^\circ\text{C}$.

Components separated	Separation factors	
	Cation exchanger in the Cu^{2+} form	Charcoal SKT Porapak Q with 10% NiSO_4
NO/air	10.0	1.4
NO/ NO_2	3.8	0.5

tion makes it possible to raise the threshold sensitivity in the determination of NO to 0.002%.

The presence of moisture in the mixture to be separated does not deactivate the sorbent in the copper form; the retention time for water at 80°C is 20–22 min, while that for NO is 2 min. However, careful desiccation of the carrier gas (helium, nitrogen, CO_2 and other gases) is required to maintain high selectivity and prolong the working life of the sorbent with respect to nitrogen oxides.

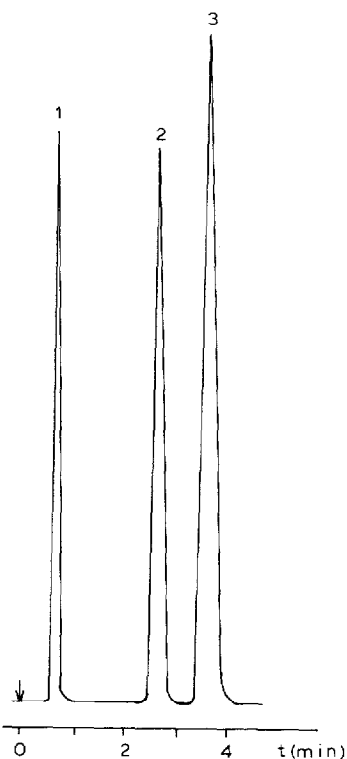


Fig. 5. Chromatogram of a gas mixture containing air (1), N_2O (2) and CO_2 (3). Sorbent: sulphite-bonded cation-exchanger in the potassium form. Column: 2.5×3 mm I.D. Temperature: 60°C . Helium carrier gas flow-rate: 30 ml/min.

The use of the macroporous sulphate-bonded cation exchanger in the potassium form is promising for identification of N_2O in the combustion products of hydrocarbon fuels containing such components as H_2 , N_2 , CO , NO , N_2O , CO_2 . The determination of N_2O in the presence of high carbon dioxide concentrations is one of the difficult problems of GC. Its solution requires the elution of N_2O before CO_2 . Conventional sorbents such as charcoal, Porapak Q, Synachrom, coupled columns with silica gel and Ceolytes fail to provide the required elution order, and CO_2 is eluted before N_2O .

Nitrous oxide is eluted before CO_2 on Porapak T columns but the selectivity of the separation is insufficient ($k = 1.04$). The required elution order and higher selectivity may be achieved by use of a sulphate-bonded cation exchanger based on the copolymers of styrene and divinylbenzene, and in the forms K^+ and Cs^+ (Fig. 5). The gases N_2O and CO_2 were separated using a Tsvet Model 132 gas chromatograph with a thermal conductivity detector, on $2.5\text{ m} \times 3\text{ mm}$ I.D. columns at 60°C and using helium as carrier gas at a flow-rate of 30 ml/min. The separation factor for the N_2O - CO_2 mixture is 1.40, while it is 0.74 on Porapak Q, 1.04 on Porapak T and 0.63 on charcoal SKT. The large difference between the retention of N_2O and CO_2 permits the detection of nitrous oxide contents as low as 0.05–0.20% in the presence of high carbon dioxide concentrations.

Thus, the use of macroporous cation exchangers in GC enables one to accomplish previously impracticable separations.

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