

heated to 900°. Since the thermoanalytical studies indicate that the water in apatites is not chemically bound, the peak at 1635 cm<sup>-1</sup> may be considered to be characteristic of adsorbed water.

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### Calcium Complex Grease as a Suitable Substrate for Gas Liquid Chromatography

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Calcium complex grease has been evaluated for its suitability as a stationary phase for GLC. It elutes symmetrical peaks within short time and can successfully be used up to 250° with negligible bleed. Qualitative and quantitative results are obtained with this grease for several test mixtures. Data on relative retention time for various solutes with respect to *n*-hexane are also reported.

CONSIDERABLE work has been done on solvent efficiency of a variety of greases used as stationary phase in gas liquid chromatography (GLC)<sup>1,2</sup>. Present investigation was undertaken to study the solvent efficiency of calcium complex grease in GLC.

The wheel bearing grease which is available in the market was used as a substrate for GLC columns. The physico-chemical properties were first examined. The general *n-d-M* methods<sup>3</sup> along with IR spectroscopy<sup>4</sup> revealed the presence of 80% petroleum oil as the fluid (paraffins 78%, aromatics 17% and naphthenes 5%) and 20% soap as the thickener (calcium acetate + calcium stearate). Thermal stability of the grease was examined by thermogravimetric analysis indicating a loss of 2% at 250° and 5% at 300°, beyond which the decomposition started. Therefore, it can be used up to 250° safely.

Three columns with different loading of the grease and with varying parameters were prepared and

used after conditioning them for 24 hr at 250° with nitrogen flow rate 80 ml/min. Beckman GC-2A gas chromatograph having thermal conductivity detector coupled with a Bristol 1 mV recorder was used. All the chemicals used were of extra pure quality (Polyscience Corporation, USA).

The behaviour of this phase, appeared satisfactory in terms of theoretical plate concept. Since the liquid phase must possess a solvent activity and should exhibit a differential solubility for solutes. The solvent efficiency of calcium complex grease on chromosorb 'W' 60/80 mesh, acid washed coiled stainless steel column (2 m × 4.5 mm) was determined for various compounds and the data are presented in Table 1.

Few standard mixtures were quantitatively evaluated on this phase by usual methods. The calculated values were in close agreement with the values known for standard mixtures. The elution curves from the calcium complex grease columns are sharp and symmetrical for diverse types of solutes. Separation of consecutive peaks can be measured from these chromatograms in terms of resolution<sup>5</sup>, which measures both the column and solvent efficiency. Some special features of this phase for practical purposes have been studied. Low coating of the phase in a short column exhibited fast analysis of high boiling compounds, indicating the possibilities of its usefulness in resolving higher members in a homologous series. Chromatograms recorded at 140° on a short column (1 m × 4.5 mm)

TABLE 1 — RETENTION DATA ON 10% CALCIUM COMPLEX GREASE

Sl No.	Solutes	b.p., °C (760 mm)	Retention relative to <i>n</i> -hexane
1	<i>n</i> -Pentane	36.1	0.45
2	<i>n</i> -Hexane	68.7	1.00
3	<i>n</i> -Heptane	98.4	1.97
4	<i>n</i> -Octane	125.6	4.18
5	<i>n</i> -Decane	174.0	17.94
6	2,4,4-Trimethyl pentene-1	101.4	2.21
7	2,4,4-Trimethyl pentene-2	104.9	3.21
8	3,5,5-Trimethyl-1-hexene	—	7.71
9	Benzene	80.1	2.00
10	Toluene	110.6	4.29
11	Ethylbenzene	136.2	8.08
12	( <i>p</i> + <i>m</i> )-xylene	138.4	8.93
13	<i>o</i> -Xylene	144.4	10.71
14	Cumene	152.4	11.94
15	Mesitylene	164.7	18.71
16	Dichloromethane	40.0	0.64
17	Chloroform	61.0	1.43
18	Carbon tetrachloride	76.8	1.86
19	Ethyl acetate	77.2	0.79
20	Nitromethane	101.3	0.71
21	Pyridine	115.3	3.57
22	Methanol	64.7	0.21
23	Ethanol	78.5	0.34
24	Isopropanol	82.3	0.43
25	<i>n</i> -Propanol	97.2	0.73
26	Isobutanol	108.4	1.29
27	<i>n</i> -Butanol	117.7	1.71
28	Cyclohexane	80.7	1.71
29	Formaldehyde	—	0.21
30	Water	100.0	1.36
31	Acetone	56.5	1.43
32	Methyl ethyl ketone	79.6	0.86

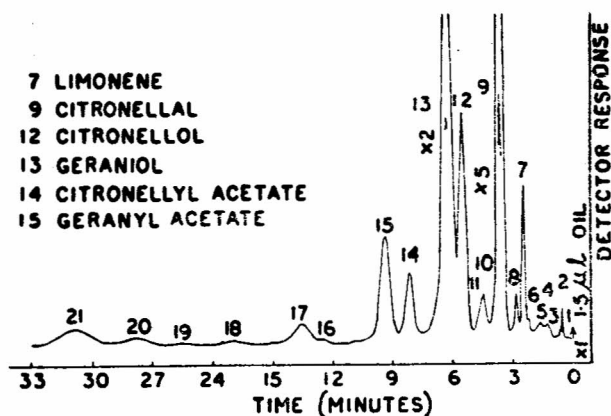


Fig. 1 — Separation of Java citronella oil [Column = 2 m  $\times$  4.5 mm; packing = 10% calcium complex grease on chromosorb 'W' (60/80 mesh); temp. = 160°]

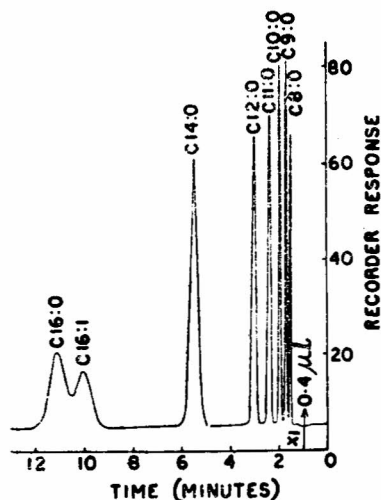


Fig. 2 — Separation of methyl esters of fatty acids [Column = 2 m  $\times$  4.5 mm; packing = 10% calcium complex grease chromosorb 'W' (60/80 mesh); temp. = 210°]

with 2% coating showed good separation of *n*-paraffins, ranging from C<sub>14</sub> to C<sub>16</sub> within 6 min and of  $\alpha$ -olefins from C<sub>9</sub> to C<sub>12</sub> within 4 minutes. This phase seems to be of great utility for the routine analysis of higher boiling compounds and if used with temperature programming can cover wide range.

An advantage of this phase was noted while comparing its performance with carbowax 20M, the most widely recommended phase for the analysis of essential oils. In contrast to carbowax 20M, calcium complex grease (Fig. 1) could resolve citronellol from geranyl acetate from the oil of Java citronella (*Cymbopogon winterianus*) under identical operating conditions with equivalent liquid phase loading. Methyl esters up to C<sub>16</sub> acids were also separated using this phase within 11 min; worth mentioning is the separation of C<sub>16</sub>:0 from C<sub>16</sub>:1 at an isothermal temperature (Fig. 2).

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### Micellization of Cobalt Myristate, Palmitate & Stearate in Organic Solvents

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The solubility of cobalt myristate, palmitate and stearate in organic solvents has been determined employing <sup>58</sup>Co as a tracer. The cobalt soaps have been found to be sparingly soluble. The effect of temperature on the solubility has also been studied and data obtained have been used for the determination of critical micelle concentration (c.m.c.) and critical solution temperature (C.S.T.) of the soaps. It has been observed that C.S.T. value decreases and c.m.c. value increases from cobalt stearate to myristate.

In earlier publications<sup>1,2</sup> from our laboratory the solubility method was employed to very low critical micelle concentration (c.m.c.) values of metal soaps in organic solvents. The difficulty in determining the low solubility was overcome by employing radio-tracer technique. As an extension the solubility and micellization of cobalt soaps in organic solvents using radioactive <sup>58</sup>Co as a tracer have now been determined.

Potassium myristate, palmitate and stearate were prepared as reported<sup>3</sup>. All other reagents were of AR grade. Radioisotope <sup>58</sup>Co in the form of cobalt chloride in dil. HCl solution was obtained from Isotope Division, BARC, Bombay. Solvents were either of AR grade or otherwise purified by standard methods. Labelled cobalt soaps were prepared in the same way as labelled cadmium soaps<sup>1</sup>. Standard solution of cobalt soap was prepared by dissolving a weighed amount of the soap in known volume of benzene-methanol (1:1) in which it was found to be

TABLE 1 — SOLUBILITY OF COBALT SOAPS AT 30°  $\pm$  0.5°

Solvents	Stearate $\times 10^5$ (mole/litre)	Palmitate $\times 10^5$ (mole/litre)	Myristate $\times 10^5$ (mole/litre)
Benzene	0.79	1.41	1.68
Toluene	0.34	0.50	1.73
<i>m</i> -Xylene	1.07	1.47	2.01
Chlorobenzene	0.36	1.21	1.39
Nitrobenzene	0.33	0.32	0.90
Dioxane	1.08	1.51	2.12
Acetone	0.28	0.47	0.69
Ethyl methyl ketone	1.13	1.94	2.57
Chloroform	0.59	1.40	1.51
Dimethylsulphoxide	1.18	1.45	1.63
Dimethylformamide	1.02	1.83	1.87
Water	0.42	0.96	1.74

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