

SHORT COMMUNICATION

**SEPARATION BY SELECTIVE ADSORPTION: PREPARATIVE
LIQUID CHROMATOGRAPHY**

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RINGKASAN: *Suatu penyelidikan untuk memisahkan campuran metil ester serta metil isostearat menggunakan teknik penjerapan kepilih fasa cecair telah berhasil. Teknik tersebut dapat menjadi penggerak untuk kegunaan dalam teknologi arus berlawanan tersimulasi. Didalam penyelidikan ini teknik kromatografi cecair tersedia menggunakan beberapa bahan penyahjerap telah diuji pada keadaan pemisahan yang berlainan (pembolehubah: suhu dan masa pensampelan). Nilai maksimum komposisi jumlah metil isostearat yang terpisah ialah 81%. Nilai tersebut diperolehi dengan menggunakan n-heptana +1% asid asetik pada suhu 30°C. Kadar penyahjerapan bahan larut telah didapati dipengaruhi oleh suhu serta jumlah asid asetik atau etil asetat yang dicampur kepada n-heptana sebagai bahan penyahjerap.*

ABSTRACT : An investigation to separate methyl isostearate from a mixture containing methyl esters and methyl isostearates using the isothermal liquid phase selective adsorption technique proved to be successful. The technique may provide the impetus for use in simulated counter current technology. This particular investigation utilized the method of preparative liquid chromatography using several desorbent materials and separation conditions (temperature and sampling time). The maximum percentage composition of methyl isostearate separated was 81.1%. This value was obtained using n-heptane +1% acetic acid as desorbents at 30°C. The solute desorption rates were found to be influenced by both temperature and the percentage of the acetic acid or ethyl acetate added to n-heptane as desorbents.

KEYWORDS : Isostearate separation, preparative liquid chromatography, n-heptane + acetic acid desorbent.

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INTRODUCTION

The development of a reliable and commercially adaptable technique for the continuous separation of fine chemicals would be a significant contribution to the petrochemical and biotechnology-based industries. A technique that has been investigated as a possible method is the continuous isothermal liquid-phase adsorptive separation technique developed and patented by UOP, Broughton, 1968. The technique is perhaps more well known by its patented name, SORBEX. This particular method has been utilized in a number of separation processes by several researchers (Broughton, 1968; de Rosset and Neuzil, 1972; Stine and Broughton, 1965; Broughton and Gerhold, 1961). The Simulated Counter Current (SCC) technology, is based on very simple foundations and the challenge lies in the actual operating system.

A possible application of the SCC technology is in the separation of branched-chain carboxylic acids from a mixture of straight and branched-chain carboxylic acids. Previous studies which applied the SCC technology in various separation processes include the separation of :

- i) An ester of an unsaturated fatty acid from a mixture containing esters from both. The saturated and the unsaturated acids (Neuzil and de Rosset, 1977a);
- ii) A saturated fatty acid from a mixture containing both the saturated and unsaturated fatty acids (Cleary *et al.*, 1985);
- iii) An ester of a monoethanoid fatty acid (Neuzil and de Rosset, 1977b) and;
- iv) An ester of a polyethanoid fatty acid (de Rosset and Neuzil, 1978).

However, to date, no work has been reported on the separation of isomers of fatty acids. This work was undertaken to investigate the feasibility of separating methyl isostearate from a mixture of methyl esters and methyl isostearates. A preparative liquid chromatography (PLC) system was used to perform the separation.

MATERIALS AND METHODS

The following were investigated :

- i) Testing of silica as a suitable adsorbent material.
- ii) The suitability of desorbent materials.
- iii) The effect of different separation conditions on the separating ability.

The separation was effected on a PLC system as shown in Figure 1. The system was able to facilitate the ease of changing adsorbent and desorbent materials for testing and registering temperature of separation, as well as to measure the flow rates of the mobile phase and the feed composition.

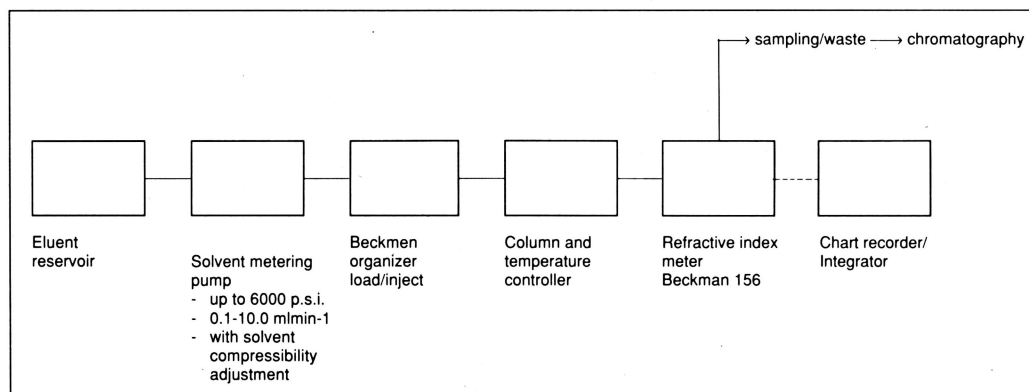


Figure 1. Schematic representation of the preparative liquid chromatography (PLC) system

All the actual runs and run conditions are summarised in Tables 1A and 1B. Some samples from the PLC system were further analysed on a gas chromatograph (GC) for greater sensitivity of detection. The conditions for GC detection were:

Injection	=	10 μ l
Final and initial temperature	=	200°C
Programme rate	=	0.0°C/min
Run time	=	25 min

RESULTS AND DISCUSSION

Calibration of the retention times on the PLC and the GC systems showed that:

- i) On the PLC system, the methyl stearates were eluted within 22 ± 0.05 min while the isostearates eluted at 36.73 ± 0.05 min;
- ii) On the GC system, the methyl stearates were eluted within 15-16 min, whilst the isostearates eluted within 17-18 min.

Table 2 shows that the results obtained in Run 1 were not very useful, as retention times of the components were found to be too close. Peaks were too close to the starting point, indicating either a fast solute desorption rate, or a strong desorbent adsorption onto the desorbent.

Table 1A. Runs without further GC sampling to test desorbent suitability and effect of temperature

Run	Materials	Run kind	Run conditions		
			Temp (°C)	Feed composition	Flow rate (ml/min)
1	Acetone + A Acetone + B	Desorbent Suitability	30	Acetone + A Acetone + B	0.4
2	n-heptane + 2% ethyl acetate	Desorbent Suitability	30	50%D + 50% (A:D) 50%D + 50% (B:D) 50%D + 50% (A:B)	0.4
3	n-heptane + 4% ethyl acetate	Desorbent Suitability	30	50%D1 + 50% (A:B)	0.4
4	n-heptane + 4%	Desorbent Suitability	30	n-heptane + 4% acetic acid 50%D2 + 50% (A:B)	0.4
5	Desorbent: n-heptane + 2% ethyl acetate	Effect of temperature	30, 35 60, 70	50%D + 50% (A:B)	0.4

Table 1B. Runs with further GC sampling to test desorbent suitability and effect of temperature

Run	Materials	Run kind	Run conditions		
			Temp (°C)	Feed composition	Flow rate (ml/min)
6	n-heptane + 2% acetic acid (Test for sampling time)	Desorbent Suitability	30	50%D2+50%(A+D2) 50%D2+50%(B:D2) 50%D2+50%(A+B)	0.4
7	n-heptane+1% acetic acid	Desorbent Suitability	30	50%D3+50%(A+B)	0.4
8	n-heptane+2% acetic acid	Effect of temperature	30,35 60,70	50%D2+50%(A+D2) 50%D2+50%(B:D2) 50%D2+50%(A+B)	0.4

Material Description

A : 1% mixture of methyl esters

B : 1% methyl isostearates

D : n-heptane + 2% ethyl acetate

Absorbent Material: silica (Biorad 21663 R sil silica D column)

D : n-heptane + 4% ethyl acetate

D2 : n-heptane + 2% acetic acid

Source : IFP Rueil

In Run 6 (Table 1B), a test was carried out to investigate the effect of sampling time on retention time, n-heptane + 2 % acetic acid was taken as the desorbent. The results are tabulated in Table 2. It was observed that the best separation was at a sampling time of 27-30 min. This value was taken for all further runs.

Table 2. Effect of sampling time on retention time (RT)

Run	Sampling time (min)	RT (min)	Comments
1	6-10	-	No major peaks
2	10-27	6.29,7.61,9.51,12.01, 12.81,15.65 & 18.03	Separation not amenable
3	27-30	15.08,17.95,30.67	Separation effected well

Table 3 shows studies using n-heptane + 2% ethyl acetate (Run 2), where a separation between the methyl and isostearates is observed; iso RT 36.73 - 36.47 min, while for normal stearates an RT of less than 22 min is seen. When the acetate percentage was doubled (Run 3), the RT of the iso peak decreased to 24.39 min from 36.47 min, showing a faster desorption rate. In studies using n-heptane + acetic acid as desorbents (Runs 4, 6 and 7) separation was observed at its best at 1.0% acetic acid content in the desorbent. When the acetic acid component was 4%, the separation time between the methyl and the isostearates was found to be very small; 3.13 min. As the acetic acid component increased a simultaneous decrease in separation time was observed. When comparing n-heptane + 2% ethyl acetate and n-heptane + 2% acetic acid, the latter appeared to be a better desorbent because under the same conditions, the acetate desorbent desorbed faster.

Doubling the acetate (4% ethyl acetate) and acetic (4% acetic acid) fractions showed a decrease in retention times (Table 3). The separation, however, was better with the n-heptane + 4% acetic acid compared to n-heptane + 4% ethyl acetate. The peaks (from raw data) of elution also showed that the % areas from the acetic acid fractions tended to be higher indicating more fractions eluted per % volume. The raw data, not included in this paper, has been reported elsewhere (Wan Mohtar and Lonchamp, 1991). In the study involving the effect of temperature on separation conditions (Runs 5 and 8), n-heptane + 2% ethyl acetate and n-heptane + 2% acetic acid were used (Table 4). It was observed that an increase in temperature of run conditions resulted in an increase in desorption rates for both desorbents. The separation difference also shifted and was not affected by the increase in temperature. The optimum temperature of operation was 30°C.

Table 3. Results of runs with the selected desorbents and run conditions

Run	Desorbent	Component in feed	RT's of major peaks (min)	Comments
2	n-heptane + 2%ethyl acetate	methyl stearates + desorbent	8.25,8.69,22.22	-
		methyl isostearates + desorbent	8.31,8.78,19.66 <u>+36.73</u>	36.73 peak an isostearate
		methyl stearates + methyl isostearates + desorbent	8.22,8.67,20.76,21.19 <u>+36.47</u>	36.47 iso peaks
3	n-heptane + 4%ethyl acetate	methyl stearates + methyl isostearates + desorbent	8.22,8.56,16.12,18.06 <u>24.39</u>	24.39 iso peak
7	n-heptane + 1%acetic acid	methyl stearates + methyl isostearates + desorbent	8.16,8.59,16.63,17.53, 19.59,23.06, <u>38.53</u>	-
6	n-heptane + 2%acetic acid	methyl stearates + methyl isostearates + desorbent	9.35,9.77,13.30,16.77, 18.97, <u>30.57</u>	30.57 iso peak
4	n-heptane + 4% acetic acid	methyl stearates + methyl isostearates + desorbent	8.34,10.54,12.90,15.65 17.64 and <u>20.77</u>	small separation between iso and linear peaks.

Table 4. Effect of temperature on separation

Temp (°C)	RT (min)	
	n-heptane + 2% ethyl acetate	n-heptane + 2% acetic acid
30	35.97	30.67
35	34.96	28.75
60	30.34	23.12
70	28.54	21.23

As a means to improve sensitivity of analysis, samples from n-heptane + 2% acetic acid (the best desorbent) were further analysed on GC. The results are given in Tables 5A and 5B. Table 5A (1% acetic acid) showed that the iso peaks were eluted at times above 12 min. Recovery of the iso C18 fraction was highest in the 1% acetic acid at 81.10% (Table 5A). These results further confirmed the C18 peaks detected using PLC.

Table 5A. Summary of results obtained from GC analysis of sample fractions

Sample No.	nC14		nC15		nC16		nC17		isoC		nC18		isoC18		% isoC18
	RT	Area	RT	Area	RT	Area	RT	Area	Rt	Area	RT	Area	RT	Area	
1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
3	6.3	451	-	-	-	-	-	-	-	-	15.25	-	-	-	-
4	6.27	3329	7.60	988	9.53	76756	12.01	5005	12.02	9736	15.25	50976	-	-	-
5	6.29	55.36	7.61	1141	9.53	55515	12.02	2060	12.81	3554	15.63	20631	-	-	-
6	6.29	1160	7.61	220	9.48	13668	12.03	493	12.82	530	15.60	5255	-	-	-
7	6.29	395	-	-	9.46	1988	-	-	-	-	15.59	398	18.04	344	5.26
8	-	-	-	-	9.46	454	-	-	-	-	-	-	17.96	592	9.38
9	-	-	-	-	-	-	-	-	-	-	-	-	18.06	4732	92.16
10	-	-	-	-	-	-	-	-	-	-	-	-	17.94	23690	81.10
11	-	-	-	-	-	-	-	-	-	-	-	-	17.84	3700	77.80
12	-	-	-	-	-	-	-	-	-	-	-	-	18.16	224	100.00
13	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Desorbents: n-heptane + 1% acetic acid

Table 5B. Summary of gas chromatograms with n-heptane + 2% acid as desorbent

Sample (min)	Sampling time	RT (min)	Comments
1	6 - 10	-	No separation
2	10 - 27	6.29, 7.61, 9.31, 12.01 12.81, 15.65, 18.03	Isostearates present as well
3	27 - 30	15.08 and 17.95	Isostearates present as well

CONCLUSION

The most important conclusion in this investigation is that it was possible to separate methyl stearates and methyl isostearates using the system described. The most promising desorbent concluded from the PLC experiments was n-heptane + 2% acetic acid with separation conditions of 30°C operating temperature and 27-30 min sampling time. Samples from the n-heptane + acetic acid run further analysed on the GC confirmed the PLC results.

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