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RECYCLE GEL PERMEATION CHROMATOGRAPHIC ANALYSIS OF OLIGOMERS AND POLYMER ADDITIVES

SHIGERU NAKAMURA, SUSUMU ISHIGURO, TSUYOSHI YAMADA and SEIJI MORIIZUMI

Central Research Laboratory, Showa Denko K.K., Tamagawa, Ota-ku, Tokyo (Japan)

SUMMARY

A recycle gel permeation chromatograph with polystyrene gel as the column packing was devised for the separation and identification of oligomers and polymer additives. The chromatograph was equipped with a differential refractometer and an ultraviolet detector.

Oligomers can be separated effectively by means of the recycle technique. Various additives in commercial resins can be separated without using the recycle technique, and the individual components can be identified by comparison of the distribution coefficient and sensitivity of the two detectors by the use of known compounds.

INTRODUCTION

The separation of oligomers and polymer additives in polymer materials has recently become so complex that an effective separation technique is required. Gel permeation chromatography (GPC), introduced by Moore[1] in 1964, is now applied not only in the determination of the molecular weight distribution of polymers, but also in the separation of organic compounds[2] and oligomers[3]. Howard[4] described the separation of polymer additives, but did not adequately cover the separation of complex mixtures into individual components. For the adequate separation of unresolved adjacent peaks, the technique of effective recycling[5–7] by using a short column, in which the sample is recycled through the same columns a number of times, can be used.

We have constructed a GPC recycling apparatus for the effective separation and identification of oligomers and polymer additives. The recycling technique was very useful for the separation of oligomers that are usually difficult to separate. It was also possible to separate various polymer additives easily without using the recycling technique. We tried to identify the polymer additives by using the distribution coefficient and the response sensivivity ratio obtained from two types of detectors.

EXPERIMENTAL

Recycle GPC

A block diagram of the GPC recycling apparatus is shown in Fig. 1.

Of course, the recycling technique was not used when the separation was already adequate.

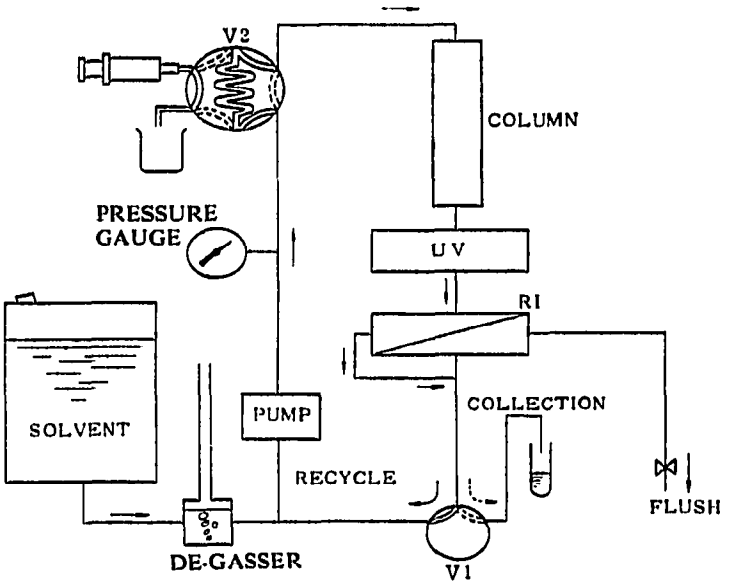


Fig. 1. Schematic diagram of recycle GPC. V1 = recycle valve; V2 = sample valve.

The apparatus and the recycling operation consisted of the following. When the original separation was not satisfactory, recycling was used. The sample was injected by means of injection valve V2 and pumped to the columns. After passing through the columns, detectors and recycle valve V1, the sample was returned to the top of the first column. The recycling operation was continued until sufficient separation of the components of interest was obtained. The separation profile was monitored by two types of detectors, continuously recording with a two-pen recorder. The separated components can be collected by turning the recycling valve to the "Collect" position.

A differential refractive index (RI) detector (Erma Optical Works Co.) and a UV absorption detector (Japan Analytical Industry Co.) were used in series with a two-pen recorder (Rikadenki Kogyo Co.). The pump used was a Milton-Roy minipump (0–180 ml/h).

Two stainless-steel columns (1.2 m × 20 mm I.D.) were packed with cross-linked polystyrene gel (a copolymer of 96% styrene and 4% divinylbenzene; particle size 45–75 μm) which had been prepared in our laboratory. The theoretical plate number of the columns was 5000. These columns can be loaded to about 200–300 mg. A sufficient amount of sample can be loaded for further GPC fraction identification, *e.g.*, by IR, UV, MS and NMR analysis.

Experimental conditions

The experimental conditions are given in Table I.

TABLE I
EXPERIMENTAL CONDITIONS

Variable	*Condition*
Columns (2)	Polystyrene gel (4% divinylbenzene), 120 cm × 2 cm I.D.
Solvent	Chloroform
Temperature	Room temperature
Flow-rate	3 ml/min
Sample concentration	0.5–5%
Sample loop	2 ml
Detector	RI (sensitivity 8×); UV

Reagent

Reagent-grade chloroform was used as the mobile phase in GPC.

RESULTS AND DISCUSSION

Oligomer separation

In the separation of oligomers, it is desirable that a homologous series should be separated into peaks of the individual components. If this can be achieved, the degree of polymerization of each peak can be estimated and the calibration curve of the oligomer of interest can be constructed without the aid of the standard materials that are widely used for the construction of GPC calibration curves, and the molecular-weight distribution of the oligomer can then be calculated.

This advantage can usually be attained by the use of the recycle technique. Fig. 2 shows an example of the separation of commercial standard polystyrene (mol. wt. 600) using the recycling technique. On a single pass through the columns,

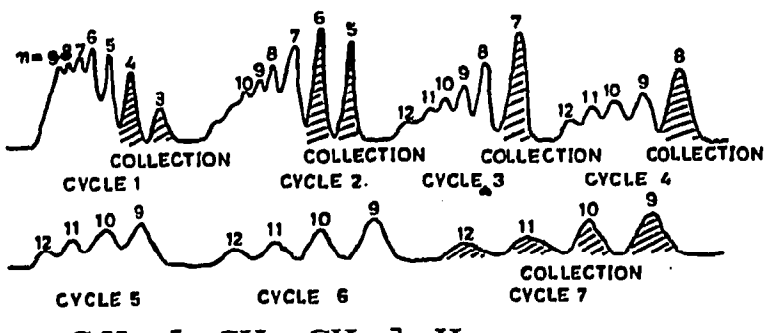
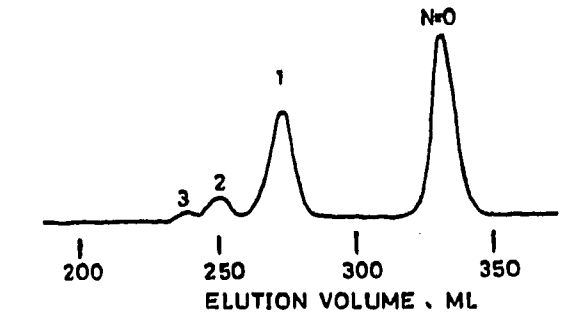


Fig. 2. Recycle chromatogram of low molecular polystyrene. Sample, standard polystyrene, mol. wt. 600.



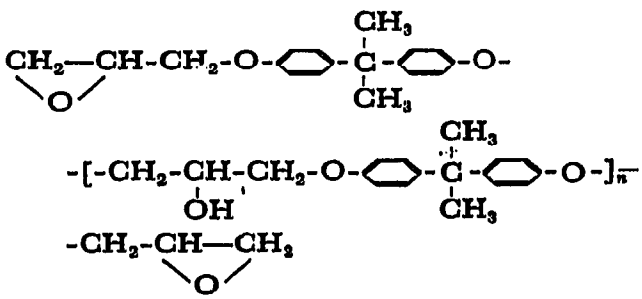


Fig. 3. Chromatogram of an epoxy resin.

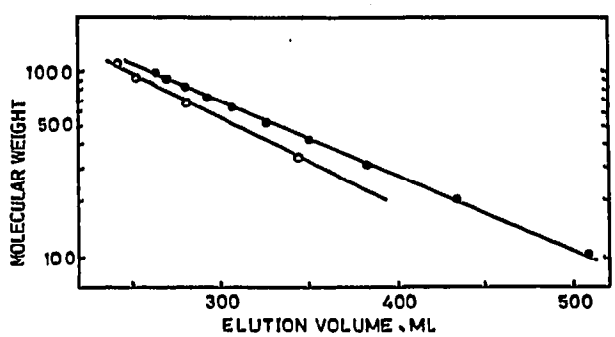


Fig. 4. Peak elution volume. Calibration graphs for polystyrene (●) and an epoxy resin (○).

peaks representing the trimers to the nonamers appeared. It was possible to collect the trimers and tetramers, as they were sufficiently resolved, and the remainder of the sample was recycled. On the second cycle, peaks of polymers up to decamers appeared, and the pentamers and hexamers were then separated and collected. Continuing in this manner, after the seventh cycle individual species of polystyrene from trimers up to dodecamers were completely separated and successfully collected.

Fig. 3 shows a chromatogram of a commercial epichlorohydrin–bisphenol A epoxy resin. In this case, the separation was adequate without the use of the recycling technique. The value of n in the structural formula shown in Fig. 3 was easily determined from the gel permeation chromatogram.

Fig. 4 shows the calibration graphs for a low-molecular-weight polystyrene and an epoxy resin.

Identification of polymer additives

Generally, the identification of GPC fractions was confirmed by additional spectrometric methods, such as IR, UV, MS and NMR spectrometry. However, for well known polymer additives, information such as the elution volume was adequate for identification in many instances. The information obtained from GPC is as follows.

Distribution coefficient. GPC permits the separation of compounds by size. A plot of elution volume against the logarithm of the molecular weight yields a straight line if the compounds to be separated are homologous. The elution volume is important in the identification of compounds, but it varies with changes in ambient temperature or with a change of syphons, so it is undesirable to compare elution volumes measured under different conditions. In this case, it is preferable to use the distribution coefficient, K_d defined as follows:

$$K_d = \frac{V_e - V_0}{V_{EOH} - V_0} \tag{1}$$

where V_e is the elution volume of the solute, V_0 is the interstitial volume of high-molecular-weight polystyrene which was excluded from the pores of the gel, and V_{EOH} is the elution volume of ethanol. Unknown compounds can be identified by comparison with the K_d values of known standard compounds. The reproducibility of the elution volume of 2,6-di-*tert.*-butyl-4-hydroxytoluene (BHT), which elutes at 412 ml, was about $\pm$ 2 ml. Elution volumes, K_d values and molecular weights of various compounds are shown in Table II.

Sensitivity ratio from two types of detectors. In this work, an RI detector and a UV detector were used to monitor solutes in the mobile phase. The sensitivity ratio, R/U, is helpful in identifying unknown compounds. R/U is defined as follows:

$$R/U = \frac{\text{Peak height from RI detector (cm)}}{\text{Absorbance from UV detector } (E)} \tag{2}$$

The R/U value provides information for qualitative analysis, and values for some polymer additives are listed in Table III.

Response direction of differential refractomer. As the RI detector monitors the differential refractive index between the eluate and the mobile phase (in this work, chloroform), the signal response is based on the difference in refractive index between the solute and the mobile phase solvent. When the refractive indices of solutes (*e.g.*, low-molecular-weight paraffins, alcohols, ketones and acids) are lower than those of the mobile phase (chloroform), the signal response is negative. As most oligomers and polymer additives have a higher refractive index than that of chloroform, the signals of their peaks are positive.

Analysis of polymer additives

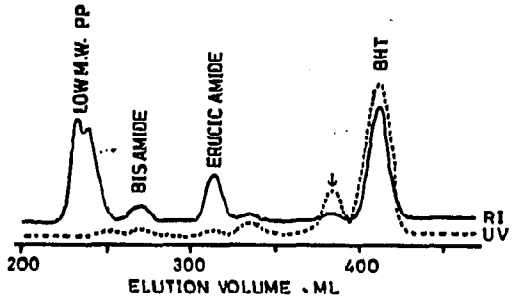
Some practical examples of the analysis of polymer additives by recycle GPC are described below.

Fig. 5 shows a chromatogram of a commercial polypropylene resin extract. A 15-g sample of polypropylene was extracted with chloroform in a Soxhlet extractor. The extract was poured into acetone in order to remove low-molecular-

TABLE II

ELUTION VOLUMES, K_d VALUES AND MOLECULAR WEIGHTS OF STANDARDS

Standard	*Molecular weight*	*Elution volume (ml)*	K_d	*Standard*	*Molecular weight*	*Elution volume (ml)*	K_d
Distearyl thiodipropionate	683	259	0.11	Santonox [4,4′-thiobis-(3-methyl-6-*tert.*-butylphenol)]	358	423	0.70
Laurylstearyl thiodipropionate	598	268	0.14	Ionol (2,6-di-*tert.*-butyl-4-methylphenol)	220	412	0.66
Dilauryl thiodipropionate	514	287	0.18	SWP [4,4′-butylidenebis-(6-*tert.*-butyl-*m*-cresol)]	383	391	0.56
Dioctyl phthalate	390	324	0.34	Topanol CA [1,1,3-tris-(5-*tert.*-butyl-4-hydroxy-2-methylphenyl)butane]	544	357	0.46
Didecyl phthalate	498	290	0.22	Irganox 565 [(4-hydroxy-3,5-di-*tert.*-butylphenylamino)-2,4-dioctylthio-1,3,5-triazine]	716	293	0.23
Dibutyl phthalate	278	358	0.47	Ionox 330 [1,3,5-trimethyl-2,4,6-tris-(3,5-di-*tert.*-butyl-4-hydroxybenzyl)benzene]	774	285	0.20
Diethyl phthalate	222	387	0.57	Irganox 1076 [*n*-octadecyl β-(4′-hydroxy-3′,5′-di-*tert.*-butylphenyl)propionate]	530	284	0.20
Dimethyl phthalate	194	410	0.65	Irganox 1010 [tetrakismethylene-(3,5-di-*tert.*-butyl-4-hydroxyhydrocinnamate methane)]	1176	244	0.04
Caprylamide	143.5	418	0.68	Phenyl-β-naphthylamine	219	493	0.96
Capramide	171.5	398	0.61	Tinuvin-P [2-(2′-hydroxy-5′-methylphenyl)-benzotriazole]	225	443	0.77
Lauramide	199.5	376	0.53	UV-24 [2,2′-dihydroxy-4-methoxybenzophenone]	245	430	0.73
Myristamide	227.5	363	0.48	UV-9 [2-hydroxy-4-methoxybenzophenone)	228	424	0.71
Palmitamide	255.5	350	0.44	Tinuvin-327 [2-(2′-hydroxy-3′,5′-di-*tert.*-butylphenyl)-5-chlorobenzotriazole]	357	385	0.56
Stearamide	283.5	339	0.40	UV-531 (2′-hydroxy-4-*n*-octoxybenzophenone)	326	355	0.45
Erucamide	337.5	318	0.32				



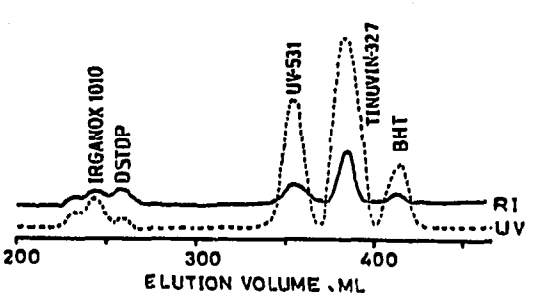


Fig. 5. Chromatogram of polypropylene resin extract.

Fig. 6. Chromatogram of a polypropylene fibre extract. DSTDP = distearyl thiodipropionate.

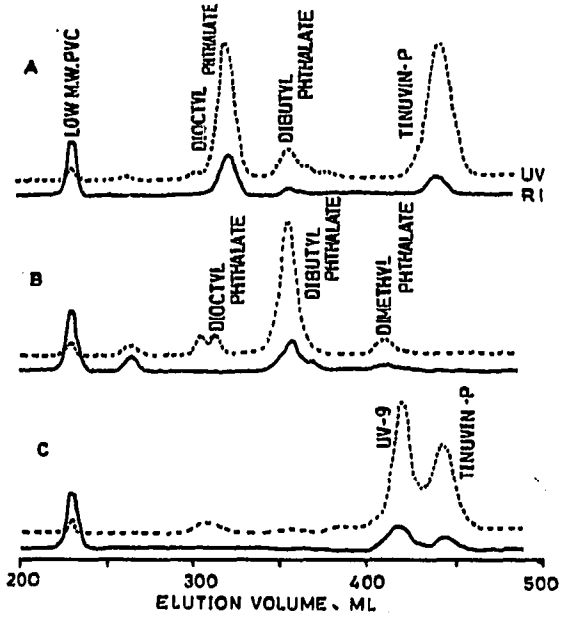


Fig. 7. Chromatograms of PVC extracts A, B and C.

TABLE III

R/U VALUES OF ADDITIVES

Additives	*R/U*
Irganox 1010 [tetrakismethylene-(3,5-di-*tert.*-butyl-4-hydroxyhydrocinnamate methane)]	26.2 ± 1.4
Irganox 1076 [*n*-octadecyl *β*-(4′-hydroxy-3,5′-di-*tert.*-butylphenyl)propionate]	24.5 ± 1.5
BHT (2,6-di-*tert.*-butyl-4-hydroxytoluene)	12.7 ± 0.6
SWP [4,4-butylidenebis-(6-*tert.*-butyl-*m*-cresol)]	10.2 ± 0.4
Distearyl thiodipropionate	540 ± 350
Dilauryl thiodipropionate	270 ± 45

weight polymer, after which it was dried and then dissolved in 5 ml of chloroform.

From the chromatogram, BHT, erucic acid and bisamide were detected, and the bisamide was identified from the IR spectrum. The peak indicated by the arrow is that of the degradation product (dimer) of BHT.

Fig. 6 shows a chromatogram of a polypropylene fibre extract. The presence of UV absorbers to which the UV detector is more sensitive could easily be deduced from the R/U value. In this case, the identification of each component was confirmed only by comparison with the elution volume or K_d value of the known compounds shown in Table II.

Fig. 7 shows chromatograms of commercially available PVC sheet extracts. A 1-g amount of PVC sheet is dipped into 10 ml of chloroform and allowed to stand overnight at ambient temperature. The extracts are chromatographed. Each component in the chromatograms was identified by comparison with the K_d values of the standard compounds.

Fig. 8 shows a chromatogram of industrial-grade lauramide and Fig. 9 shows the calibration graph for linear amides.

The equation

$$V_e = 1017 - 279 \log M \tag{3}$$

where V_e is the elution volume and M is the molecular weight of amide, can be used to calculate the molecular weights of amides. The determination of carbon numbers or molecular weights above C_{28} by the above eqn. 3 was impossible because of poor resolution, but in this case the recycling technique can be used to determine such higher amides.

Fig. 10 shows an example of the separation and identification of a commercial polymer additive, laurylstearyl thiodipropionate. In the first cycle, three components were recognized, but in view of the poor separation, recycling was carried out. After four cycles, three peaks were completely resolved and these three components were fractionated and collected. By mass spectrometric analysis, it was found that the molecular weight of peaks 1, 2 and 3 were 598, 682 and 514, respectively, and the compounds were identified as laurylstearyl thiodipropionate, distearyl thiodipropionate and dilauryl thiodipropionate, respectively.

Hitherto, the separation and determination of these components by GC were difficult because direct injection of GC causes sample degradation, and chemical

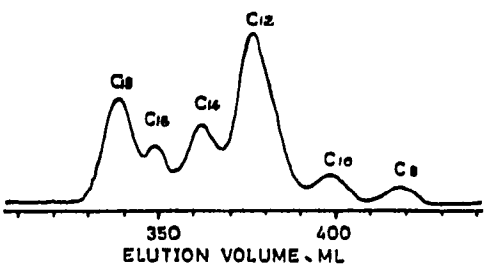


Fig. 8. Chromatogram of industrial-grade lauramide.

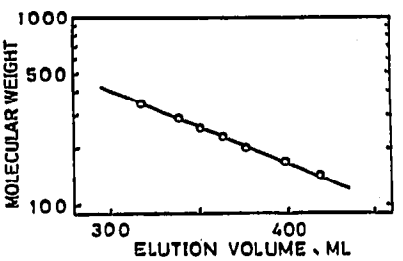


Fig. 9. Peak elution volume of amides. Calibration graph.

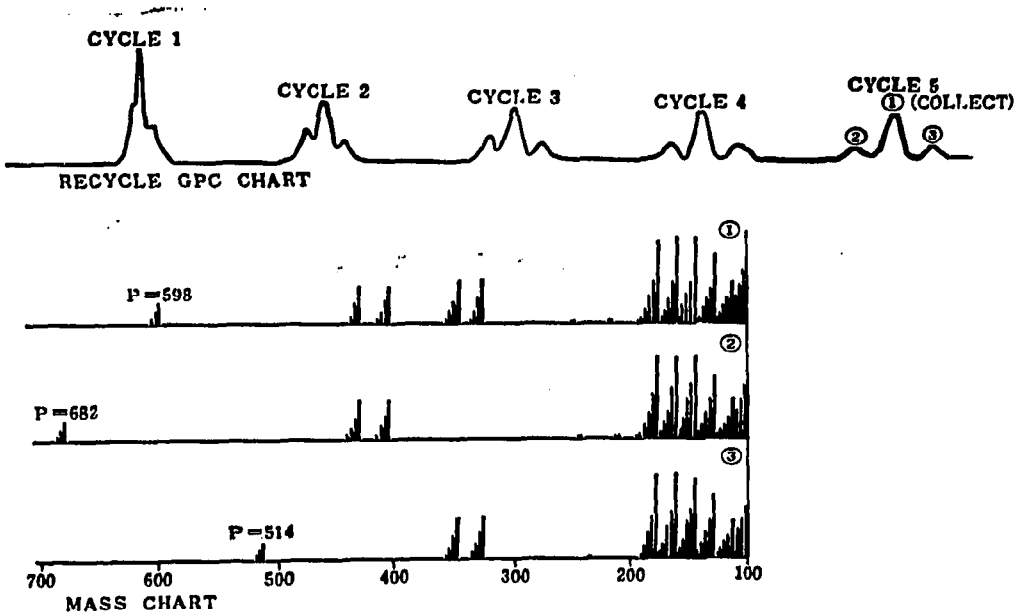


Fig. 10. Separation of (1) laurylstearyl thiodipropionate (mol. wt. 598); (2) distearyl thiodipropionate (mol. wt. 682); (3) dilauryl thiodipropionate (mol. wt. 514).

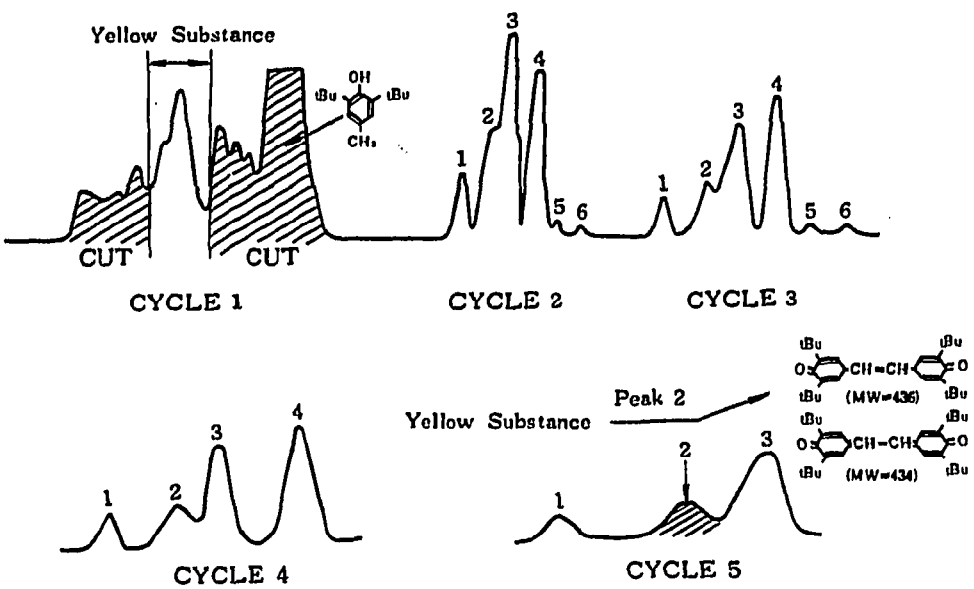


Fig. 11. Separation of yellow substances in BHT.

pre-treatment such as hydrolysis or esterification to convert them into volatile forms makes it impossible to distinguish them from one another.

Fig. 11 shows the separation of yellow oxidation products in the antioxidant BHT. This coloured component is determined by using the recycling technique. The

elution volume of the yellow component is preliminarily determined and the sample recycling region in the chromatogram is decided in order to cut off the colourless regions. The recycling and cutting off are repeated and finally only the desired component is fractionated and analyzed with a mass spectrometer. It was found that this substance is a mixture of two compounds with molecular weights of 436 and 434, as shown in Fig. 11.

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