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Development of Extraction and Separation Monitoring in Situ with On-line SFE•SFC/FTIR System

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On-line SFE•SFC/FTIR with a high pressure flow cell withstanding pressures as high as 50 MPa was built up to make an in situ observation at supercritical state. The extraction and separation efficiency determined by this system was correlated with a parameter derived from solubility parameter concept.

A supercritical fluid(SCF) can extract nonvolatile and thermolabile heavy materials without denaturation.[1)] It is difficult to make an accurate determination of solubilities of these compounds in SCF because the composition of the equilibrium SCF phase is easily shifted by both pressure and temperature on sampling. Much attention has, therefore, been drawn to the measurement in situ at supercritical state by indirect means[2)] including supercritical fluid chromatography(SFC)/fourier transform infrared spectrometry(FTIR).[3)] We report the development of on-line supercritical fluid extraction(SFE)• SFC/FTIR system which allows the rapid, precious identification of solutes extracted with supercritical carbon dioxide(SC-CO_2). Furthermore, the extraction and separation efficiency obtained by the system are correlated with a model based on a regular mixing rule.

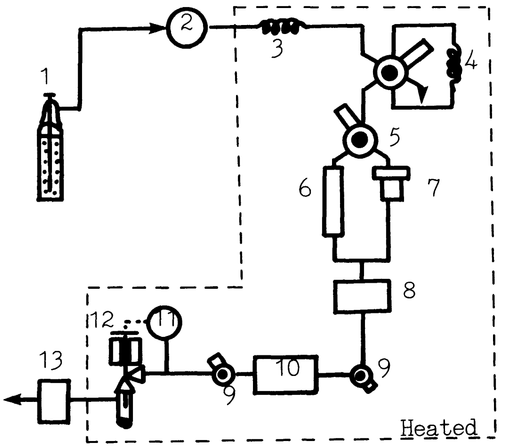

Fig. 1. Schematic diagram of apparatus used. 1:CO_2 cylinder, 2:CO_2 pump, 3: Preheater, 4:Injector, 5:3-way valve, 6:Separation column, 7:Extractor, 8:UV detector, 9:On-off valve, 10:FTIR spectrometer, 11:Pressure transducer, 12:Pressure regulator, 13:FID detector.

A schematic diagram of the system is shown in Fig. 1. Pressure control was achieved by introducing high-speed flow switching and controlling an outlet pressure irrespective of the mass flow rate of SCF.[4)] Samples were injected into the SFE•SFC system with an injection valve or extracted in a stainless steel extractor of 10 cm^3. The conventional high performance liquid chromatography(HPLC) column (150 mm long and 4.6 mm i.d.) was used for the SFC. A heated stainless steel tube of 0.25 mm i.d. was employed as the transfer tube from SFE or SFC to an IR flow cell. The mobile phase is introduced into the bottom of the cell and

Table 1. Average Extraction Efficiency(AEE) of DL-α-Tocopherol Determined by On-line FTIR at 323 K

Pressure MPa	Weight mg	Flow rate NL min^{-1}	AEE mg NL^{-1}
18.6	7.8	0.55	40.2
11.7	5.8	0.56	25.7
8.3	5.3	0.46	5.9

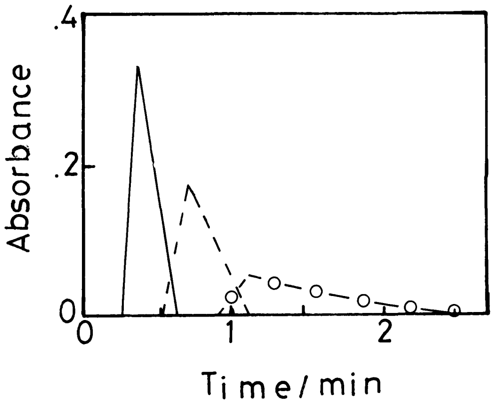

Fig. 2. The change of absorbance at 1053 cm^{-1} with time at 323 K. —:18.6 MPa, --:11.7 MPa, -o-:8.3 MPa.

emerged from the top. The stainless steel tube of 0.25 mm i.d. was connected directly to both the inlet and outlet of the cell. The infrared radiation was impinged on the cell at 90° to the flow. The selection of window material was very important for the achievement of the optimum sensitivity and adequate resolution of IR measurements at supercritical state. In this work, Ga-Gd-Garnet(GGG) window was used because the GGG material possesses the high modulus of rupture and wide useable mid-IR region(800-5000 cm^{-1}). This IR flow cell could withstand a pressure of 50 MPa by using 5 mm thick GGG windows. By comparison, to maintain a pressure of 20.7 MPa, NaCl windows would need to be 10 mm thick.[5] The cell volume was 16 μl(2 mm i.d. and 5 mm long). This cell was placed in the chamber of FTIR spectrometer equipped with a narrow band mercury cadmium telluride(MCT) detector. The interferometer scan speed was 1 scan/1.2 s. The resolution of all spectra was 4 cm^{-1}. An ultraviolet detector(UVD) and flame ionization detector(FID) were mounted in series to enhance analytical capabilities. The commercial-grade carbon dioxide was used. Nonvolatile compounds such as stearic, linolenic acid methy esters, DL-α-tocopherol and their mixtures, which were the analytical standards from Gasukuro Kogyo Inc, were used without further purification. $AgNO_3$ supported on the silica gel was used as packing for SFC.

The IR transparency of SC-CO_2 is nearly ideal, and this solvent medium is suitable for IR measurements. Although the asymmetric stretching band of CO_2 around 2350 cm^{-1} obscures the spectrum in this region, only a few compounds possess characteristic absorption bands near this wave number.

The average extraction efficiency(AEE), the average weight of solute extracted by unit volume of CO_2 during the whole course of extraction, of DL-α-tocopherol was examined as a function of pressure with the on-line SFE/FTIR. Figure 2 shows the time-course of the absorption intensity on the extraction with SC-CO_2 at 323 K±0.1 K. The absorption band at 1053 cm^{-1} is due to C-O-C stretching of DL-α-tocopherol. The time at the strongest absorption intensity, which is hereafter called a retentiom time, became longer with a reduced pressure. The variation in intensity as a function of time is considered to correspond to the change in concentration of the solute. Therefore, the amount of solute extracted with SC-CO_2 per unit volume of CO_2 can be easily calculated from the velocity of CO_2 and a weight of solute charged into an extractor in Fig. 2. Table 1 provides the AEE of DL-α-tocopherol. It is noted that the AEE is significantly enhanced with pressure above the critical pressure of CO_2. These values are close to those reported previously.[6] With the

SFE/FTIR system, the AEE of nonvolatile and heavy compounds with SC-CO_2 can be determined using a very small amount of sample.

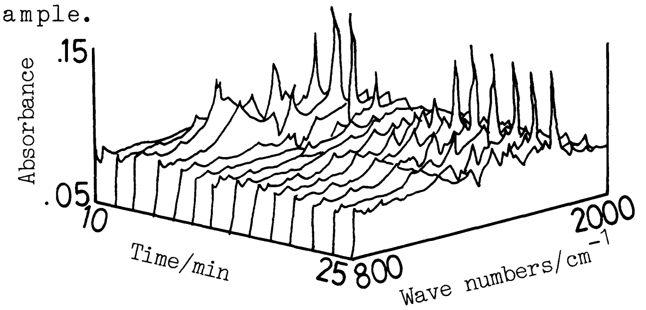

Fig. 3. The change of FTIR spectra with time on separation of a mixture of stearic and linolenic acid methyl esters with SC-CO_2 at 14.7 MPa using $AgNO_3$ supported on silica gel column.

Table 2. Retention Time of Each Component on Separation of a Mixture of Linolenic and Stearic Acid Methyl Esters with SC-CO_2 at 323 K Using $AgNO_3$ Supported on Silica Gel

Pressure	Retention time			T_{li}/T_{st}
	Linolenic	Stearic	Chloroform	
MPa	min	min	min	
18.6	15.4	9.2	1.3	1.78
14.7	21.0	12.2	1.3	1.81
12.7	30.1	16.7	1.4	1.88

In order to investigate the influence of pressure on separation performance of the SFC/FTIR system, a mixture of 0.3 mg stearic and 0.3 mg linolenic acid methyl esters in 10 µL chloroform was injected from an injection valve into the SFC/FTIR system. The flow rate of CO_2 was 0.5 NL/min(1 NL=1 L of gas at 293 K and 101.3 kPa). $AgNO_3$ (0.1 wt.%) supported on silica gel was used as a packing because a mixture of fatty acids with different degree of unsaturation could not be separated well using only silica gel as a packing.$^{7)}$ Figure 3 shows the change of FTIR spectra with time at 14.7 MPa and 323 K. The absorption band at 1744 cm^{-1} due to >C=O stretching of fatty acid methyl ester showed the major two peaks at 12.2 and 21.0 min, respectively. This result indicates that the mixture of stearic and linolenic acids can be separated well, which may be due to the difference in affinity between stearic and linolenic acid methyl esters for $AgNO_3$ supported on silica gel. The latter peak can be assigned to linolenic acid because $AgNO_3$ has a stronger affinity for fatty acids with higher degree of unsaturation.$^{7)}$ This was also confirmed by the on-line FID. Table 2 provides the retention time of chloroform, stearic and linolenic acid methyl esters on separation at 323 K. The identification of chloroform was made with C-Cl stretching of the absorption band at 1219 cm^{-1}. The retention time was longer with a decrease in pressure, but the separation efficiency was improved. This was in agreement with the results reported previously.$^{7,8)}$ The separation behavior could be confirmed in real time by the FTIR. The retention time is influenced by a linear velosity of CO_2, and for comparison it must be normalized by the retention time of chloroform as reference in such a way that $T_j=(t_j-t_{ref})/t_{ref}$, where t_j is the retention time of the component j and subscript ref indicates chloroform. Thus, the separation efficiency between the components i and j is defined as $T_i/T_j(T_i>T_j)$.

We express the affinity of the solutes for the mobile(SC-CO_2) and stationary phases by the following model. The capacity factor, k, used as a basic retention parameter, can be represented as the ratio of the activity coefficients of the solutes in the mobile and stationary phases. According to the regular mixing rule, the capacity factor(k_i) of the solute(i) is given as

$$\ln k_i = V_i(\delta_{co2}+\delta_s-2\delta_i)(\delta_{co2}-\delta_s)/RT+\ln (n_s/n_{co2}), \qquad (1)$$

where R is gas constant, δ solubility parameter, V molar volume, and n the number of moles in the column. The subscript s indicates stationary phase. The solubility parameter of SC-CO_2 was determined by the previous method.[9)] The capacity factor can represent the chromatographic retention power of the solute at supercritical state. We attempted to correlate the relative retention with $\ln(k_i/k_j)$ as previously used[10)] and with a new parameter of $\ln (k_i/k_j)/\ln k_{ch}$. If we can presume that the solubility parameter of 0.1 wt.% $AgNO_3$ supported on silica gel is 16.5 $cal^{-1/2}cm^{-2/3}$ with the assumption that the δ_s is nearly proportional to the mole fractions of uncoated silica gel and Ag, as shown in Fig. 4, a good correlation can be obtained with the new parameter using the capacity factor of chloroform(k_{ch}) but not with the previous parameter. The specific affinity of $AgNO_3$ for higher unsaturated fatty acids in SC-CO_2 may be expressed well by the coefficient $\ln (k_{li}/k_{st})/\ln k_{ch}$.

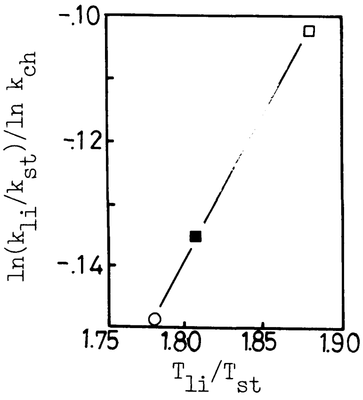

Fig. 4. Relationship between $\ln(k_{li}/k_{st})/\ln k_{ch}$ and T_{li}/T_{st}. ○:18.6 MPa, ■:14.7 MPa, □:12.7 MPa.

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