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Analysis of Insecticides and Fungicides Employing Supercritical CO_2 and Modifiers

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During its relatively short existence, supercritical fluid chromatography (SFC) has become an attractive alternative to GC and LC in certain industrially important applications. SFC gives the advantage of high efficiency and allows the analysis of non-volatile or thermally labile mixtures. Some applications of SFC to the separation of pesticides and fungicides are featured in this paper, along with representative chromatograms. Pesticide analysis has received much attention because of the environmental impact of pesticides and fungicides and the need to monitor their levels and those of their metabolites in complex sample matrices such as foods. GC often is the analytical method of choice because of the availability of sensitive, selective detectors (FPD, NOD, ECD). However, difficulties arise when the solutes cannot be analyzed by GC because of thermal instability. HPLC is not helpful either, because such compounds cannot be detected easily at trace levels by a UV detector or one of the other HPLC detectors. In these cases, SFC is an alternative to GC or HPLC for the analysis of pesticides. The SFC analysis of some polar pesticides using mass spectrometry as a detector has previously been reported[1]. Thermally labile carbamate pesticides were also separated by capillary SFC[2].

The ability to analyze moderately polar compounds with supercritical CO_2 is demonstrated in this paper; however, modifiers must be used. One of the most difficult problems with SFC is how polar substrates can be analyzed. Using the classification scheme of eluents by Synder[3], carbon dioxide shows a polarity similar to that of hexane. The solvent power of the eluents used in SFC may be enhanced by adding a second eluent, the so-called 'modifier' to the basic mobile phase. Separations are often performed by SFC where

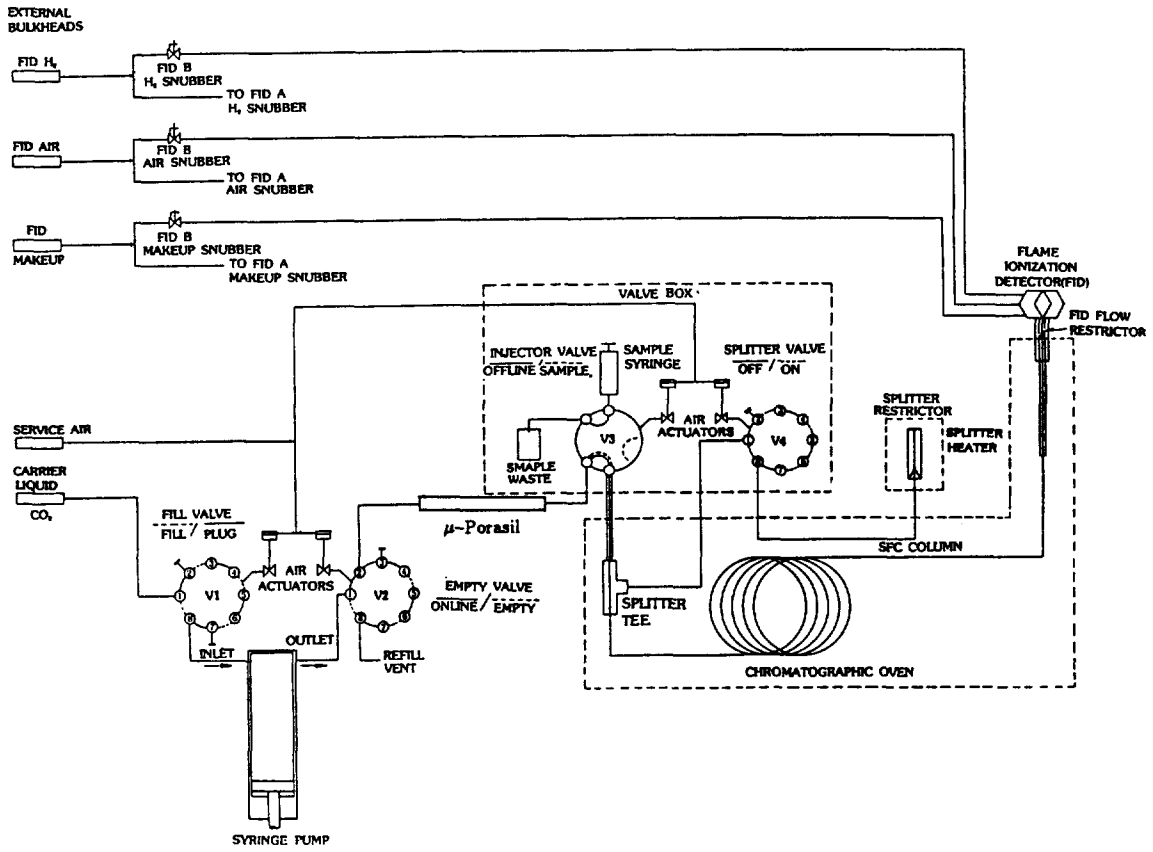


Figure 1. Overall system diagram for adding polar modifier to supercritical fluid mobile phase.

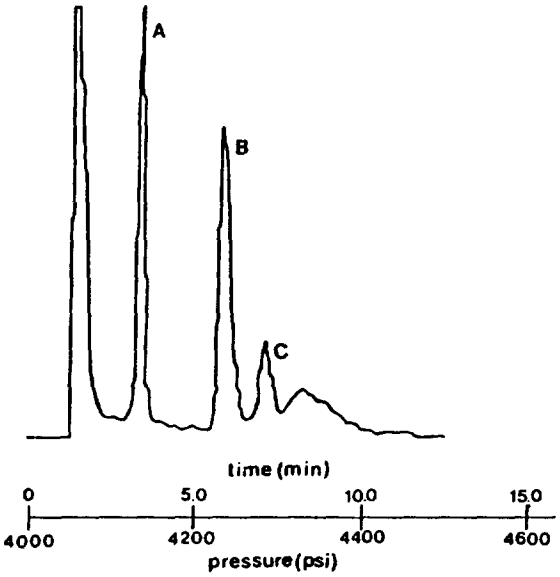


Figure 2. The chromatogram of a mixture of insecticides and fungicides. Peaks, A: Thiolix, B: Kitazine, C: Captan.

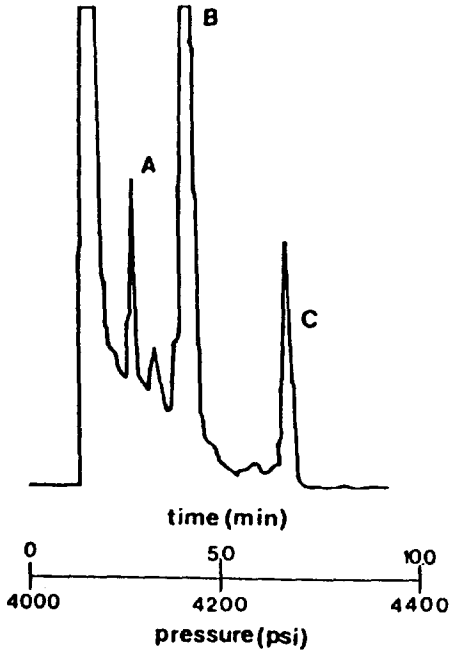
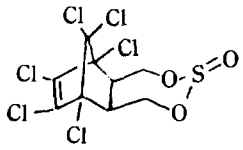
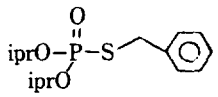
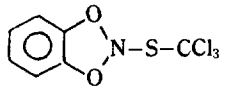
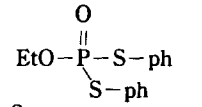
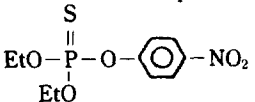
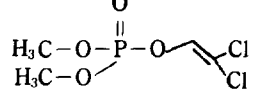


Figure 3. The chromatogram of a mixture of a mixture of insecticides and fungicides. Peaks, A: Hinosan, B: Parathion, C: DDVP.

the composition of the mobile phase is changed during the run or by adding a modifier before the chromatographic run is started. The influence on the retention behaviour of adding a modifier depends on the nature of the substrate, the stationary phase, and on the modifier itself. Yonker *et al.*,[4] report that at CO_2/methanol mixtures at 50℃ UV absorbance maxima shifts for 2-nitroanisole. When dealing with the use of modifiers, it should be mentioned that some problems arise. Frist, a binary mixture of eluents can contaminate the instrument. The modifier remaining in a injector, tubing, expecially pump can be eluted slowly during the next run. This may affect the time to achieve chemical equilibrium and cause a corrosion of the pump. Second, manyu modifiers can diffuse in the laboratory and contaminate the air in the laboratory. To overcome these problems, we designed a new method which is shown in Figure 1. Supercritical CO_2 is delivered from the pump to μ-Porasil column which is saturated with water. The μ-Porasil colum is manufactured for normal phase HPLC colunm by WATERS Co., and its func-

Table 1. The Structures of Peaks in the Chromatograms

Chromatogram	Peaks	Commercial name	Chemical mame	Structure
	A	Thiolix(Insecticide)	1,4,5,6,7,7-Hexachloro-5-norbornene -2,3-dimethanol sulfite	
Figure 2	B	Kitazine(Fungicide)	S-benzyl-0,0-diisopropyl phosphorothioate	
	C	Captan(Fungicide)	N-(trichloromethylthio) cyclohex-4-ene -1,2-dicarb-oximide	
	A	Hinosan(Fungicide)	O-Ethyl-S,S-diphenyl dithio phosphate	
Figure 3	B	Parathion(Insecticide)	O,O-Diethyl-O-4-nitro-phenylphosphor-othioate	
	C	DDVP(Insecticide)	2,2-Dichlorovinyldimethyl phosphate	

tional group is a hydroxy group (-OH). When supercritical CO_2 go through the μ-Porasil column, H_2O held on the -OH group of μ-Porasil by hydrogen bonding can dissolve in the pressurized supercritical fluids. With this method, non-polar supercritical CO_2 can have the characteristics of polar mobile phase because it can absorb polar solvent, H_2O. Therefore, after passing the μ-Porasil column, supercritical CO_2 is changed to new mobile phase with different polarity, and it is possible to separate polar samples using this new mobile phase.

Figure 2 and 3 are the chromatograms of mixtures of insecticides and fungicides using modified supercritical CO_2. Separation conditions are the follows: CO_2 at 150℃, programmed from 4000 psi to 5000 psi at 40 psi/min, diol column, FID at 300℃ restrictor flow 10 ml/min at 1500 psi. The structures of each peaks were shown in Table 1.

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