Journal of Chromatography A, 662 (1994) 323–327
Elsevier Science B.V., Amsterdam

CHROM. 25 686

Separation of T-MAZ ethoxylated sorbitan fatty acid esters by supercritical fluid chromatography

Ming Y. Ye* Kim D. Hill and Ron G. Walkup

ManTech Environmental Technology, Inc. P.O. Box 1198 Ada, OK 74820 (USA)

(First received June 23rd, 1993; revised manuscript received October 27th, 1993)

ABSTRACT

The application of supercritical fluid chromatography (SFC) to the analysis of T-MAZ ethoxylated sorbitan fatty acid esters is described. SFC separation methods utilize a density programming technique and a 50 μm I.D. capillary column. This work demonstrates that capillary column SFC is a powerful technique for the analysis of complex mixtures of many derivatives of ethoxylated sorbitan fatty acids which is not amenable to gas chromatography or gel permeation chromatography. This work also demonstrates that complex distributions of polyethylene glycol can be resolved. The results of this study show how changes in chromatographic parameters affect the SFC analysis.

INTRODUCTION

T-MAZ Ethoxylated sorbitan fatty acid esters (T-MAZ) are emulsifiers with a wide range of hydrophilic characteristics. They are used to cover a wide range of oil in water and water in oil emulsification systems. They are excellent solubilizers of essential oils, wetting agents, viscosity modifiers, antistats, stabilizers and dispersing agents. They are used to prepare numerous products in the food, cosmetic, drug, textile and metalworking industries. Because their molecules contain hydrophilic and hydrophobic moieties, T-MAZ are surface-active and concentrate at interfacial regions: oil–water, for example. They are generally referred to as surfactants. Recently, there has been considerable interest in using surfactants to remediate subsurface contamination, *e.g.* to immobilize contaminants for subsequent *in situ* treatment, to release contaminants from mineral surfaces, or redistribute immobile organic phases into the mobile aqueous phase [1–3].

T-MAZ is an industrial chemical which is a complex mixture of many derivatives of ethoxylated sorbitan fatty acids. According to the manufacturer the major component, T-MAZ 60, has a molecular mass of 1300. Because of the high molecular mass and low volatility of T-MAZ, this material is difficult to analyze by GC. High-temperature GC was used to analyze sucrose fatty acid ester fractions [4]; however, a derivatization procedure has to be performed prior to analysis. Gel permeation chromatography (GPC) is a technique used for polymer analysis to determine the molecular mass distribution. However, GPC is usually used for high-molecular-mass polymers and does not give a complete separation of all the oligomers in the polymer samples. T-MAZ does not have UV-absorbing chromophores which prohibits the use of high-performance liquid chromatography (HPLC) with UV detection. Capillary column supercritical fluid chromatography (SFC) with large solute diffusion coefficients, gas-like viscosities and liquid-like densities allows high-resolution analysis of many less volatile or labile compounds [5–8]. The greater densities of supercritical fluids compared to gases lead to elution based on solute solubility, and mobile and

* Corresponding author.

0021-9673/94/$07.00
SSDI 0021-9673(93)E1151-O

stationary phase selectivity. When used with capillary columns and mobile phase density programming, many components in this complex mixture of the fatty acid esters were resolved.

EXPERIMENTAL

The SFC instrumentation is a Dionex (Sunnyvale, CA, USA) 600-D supercritical fluid/gas chromatography system which includes a syringe pump to generate the high-pressure fluid flow, a chromatograph oven for temperature control, and a data acquisition and processing system. Pressure and density programs were generated by using a Dell 486 33 MHz personal computer which allowed a variety of density gradients. Dionex data acquisition and processing system includes an advanced computer interface (ACI), a Dell 433DE computer (Dell, Austin, TX, USA) and an Epson FX-850 printer (Epson America, Torrance, CA, USA). Detection was via flame ionization detection (FID). To obtain maximum sensitivity, the hydrogen–air ratio (1:10) was optimized and the detector operated in the most sensitive range. The flow-rates were hydrogen: 30 ml/min, air: 300 ml/min and nitrogen: 25 ml/min. The detector body was heated to 390°C. Samples were introduced into the chromatographic system using a Valco (Houston, TX, USA) injector. The injection mode used was time split with the injection duration of 0.1 s. A 1-μl volume of the sample was loaded to the injector loop which has a volume of 0.5 μl. With 0.1-s time split injection, 0.3 μl (60% of 0.5 μl) sample was loaded to the SFC column. The injector was cooled at 10°C with a NesLab constant temperature circulator (NesLab, Portsmouth, NH, USA).

Separations were accomplished by using a SB-Biphenyl-30 capillary column from Dionex which is 50 μm I.D. coated with approximately 0.25 μm film thickness. The column length was 10 m. Prior to detection the supercritical fluid was decompressed and the mobile phase linear velocity controlled to approximately 1.5 cm/s by connecting the terminal end of the capillary column to a frit restrictor attached through a fused butt connector.

Supercritical carbon dioxide was used as the supercritical mobile phase. SFE-grade carbon dioxide was purchased from Scott Specialty Gases (Plumsteadville, PA, USA). T-MAZ60K POE(20) sorbitan monostearate was purchased from PPG Industries (Gurnee, IL, USA). T-MAZ is a registered trademark of PPG Industries. Polyethylene glycol standards with molecular masses of 600, 960 and 1470 were from Polymer Labs. (Foster City, CA, USA). Methanol was from Burdick & Jackson (Baxter Healthcare Corporation, Muskegon, MI, USA). All solutions were made with methanol.

RESULTS AND DISCUSSION

T-MAZ oligomers

The molecular structure of T-MAZ ethoxylated sorbitan fatty acid esters is given in Fig. 1A. The complexity of this product is mainly due to the ethoxylation of sorbitan fatty acid with various lengths of polyoxyethyl groups, $(OCH_2CH_2)_n$. One of the major components,

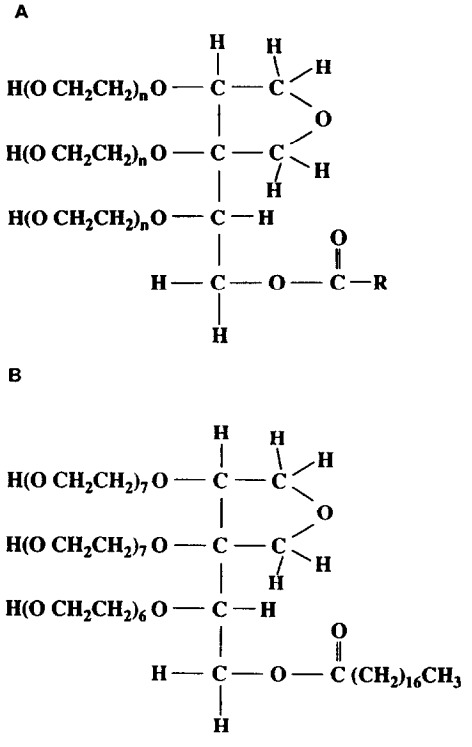

Fig. 1. Molecular structure of T-MAZ ethoxylated sorbitan fatty acid esters. (A) T-MAZ, (B) T-MAZ 60.

according to the manufacturer, is T-MAZ 60 (Fig. 1B) with total polyoxyethyl groups of 20. The molecular mass of T-MAZ 60 is about 1300. Fig. 2A shows the SFC chromatogram of T-MAZ ethoxylated sorbitan fatty acid esters, which clearly demonstrates the complexity of this product. A capillary column (10 m) with biphenyl stationary phase was used. Linear density program was taken in two steps: (1) from 0.3600 g/ml [157 atm (1 atm = 101 325 Pa), at 100°C] to 0.7000 g/ml (329 atm, at 100°C) at ramp rate of 0.01 g/ml per min and held for 20 min; (2) from 0.7000 g/ml to 0.7574 g/ml (400 atm, at 100°C) at ramp rate of 0.02 g/ml per min and then held for 50 min. The slower ramp rate of the first step allows the separation of the components in T-MAZ with the average molecular mass in the range of 1000, which will be discussed shortly.

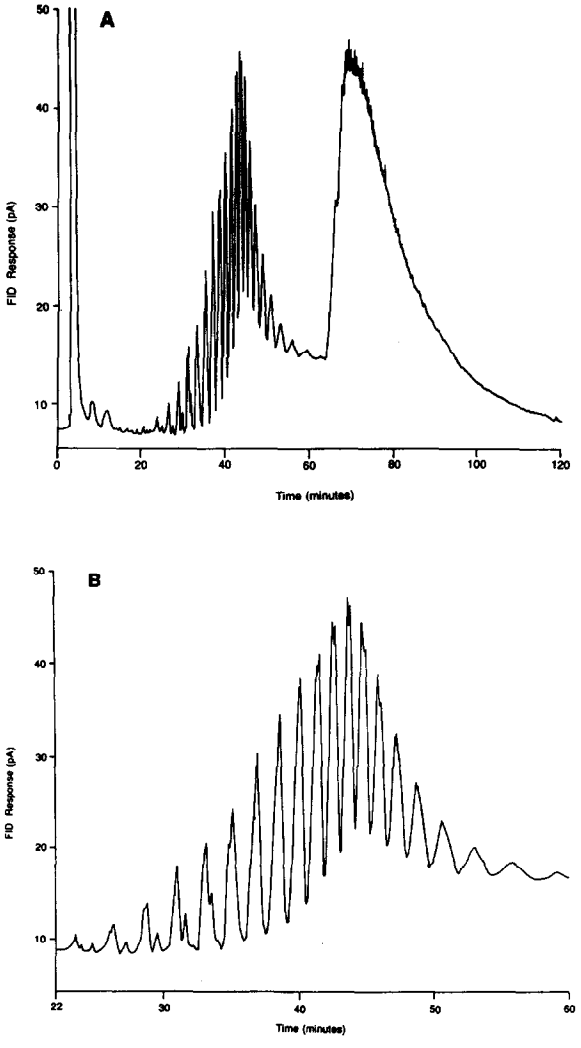

Fig. 2. SFC chromatograms of T-MAZ ethoxylated sorbitan fatty acid esters. Conditions: 10 m × 50 μm I.D. biphenyl column; CO_2 mobile phase at 100°C; Two steps linear density program: (1) from 0.3600 g/ml (157 atm, at 100°C) to 0.7000 g/ml (329 atm, at 100°C) at ramp rate of 0.01 g/ml per min and hold for 20 min; (2) from 0.7000 g/ml to 0.7574 g/ml (400 atm, at 100°C) at ramp rate of 0.02 g/ml per min and then hold for 50 min; FID at 390°C. (B) is the detail part of (A).

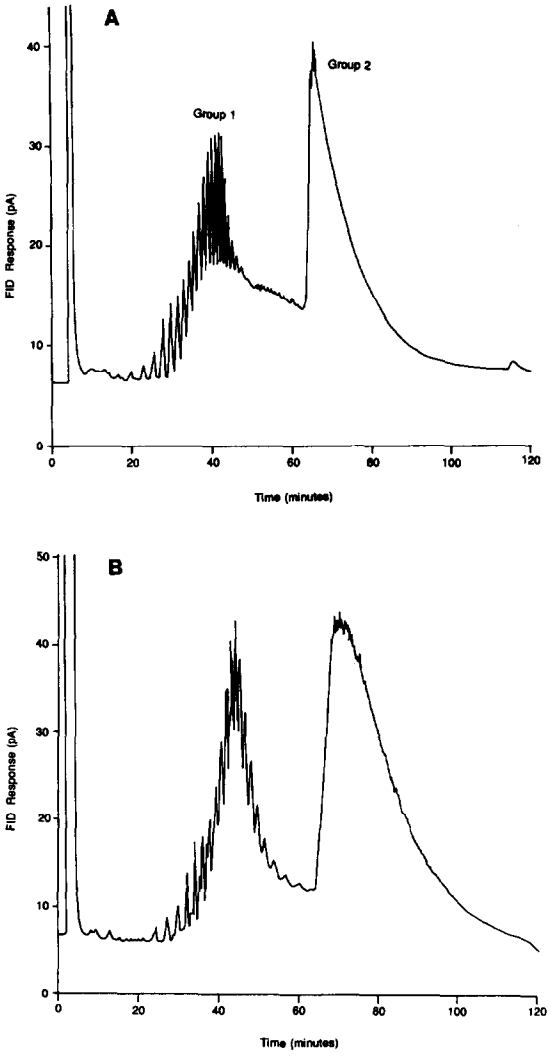

Fig. 3. SFC chromatograms of T-MAZ ethoxylated sorbitan fatty acid esters run under similar conditions except for oven temperature (A) at 80°C and (B) at 110°C, multi-step linear density program.

The column was kept at temperature of 100°C. The detail part of the chromatogram in Fig. 2A is shown in Fig. 2B. The chromatogram shows the distribution of 22 groups of oligomeric isomers eluting between 22 and 60 min. When this T-MAZ sample was analyzed by GPC, only one peak was observed [9]. The separation was also performed at 80°C and 110°C, shown in Fig. 3A and B. At 80°C the oligomers were not resolved as well as that at 100°C, and a lower ratio of peak area of group 1 and group 2 was observed, which suggests that there were more oligomers eluted at later time. This can be attributed to the lower solvating power of supercritical carbon dioxide at 80°C than that at 100°C. At 110°C, the peak resolution was significantly reduced (Fig. 3B). The experiment was also carried out at a lower FID temperature, 350°C, and the result indicated that the detector response for later-eluting peaks (high-molecular-mass components) was 20 to 40% lower at 350°C than that at 390°C. This is probably due to the condensation of

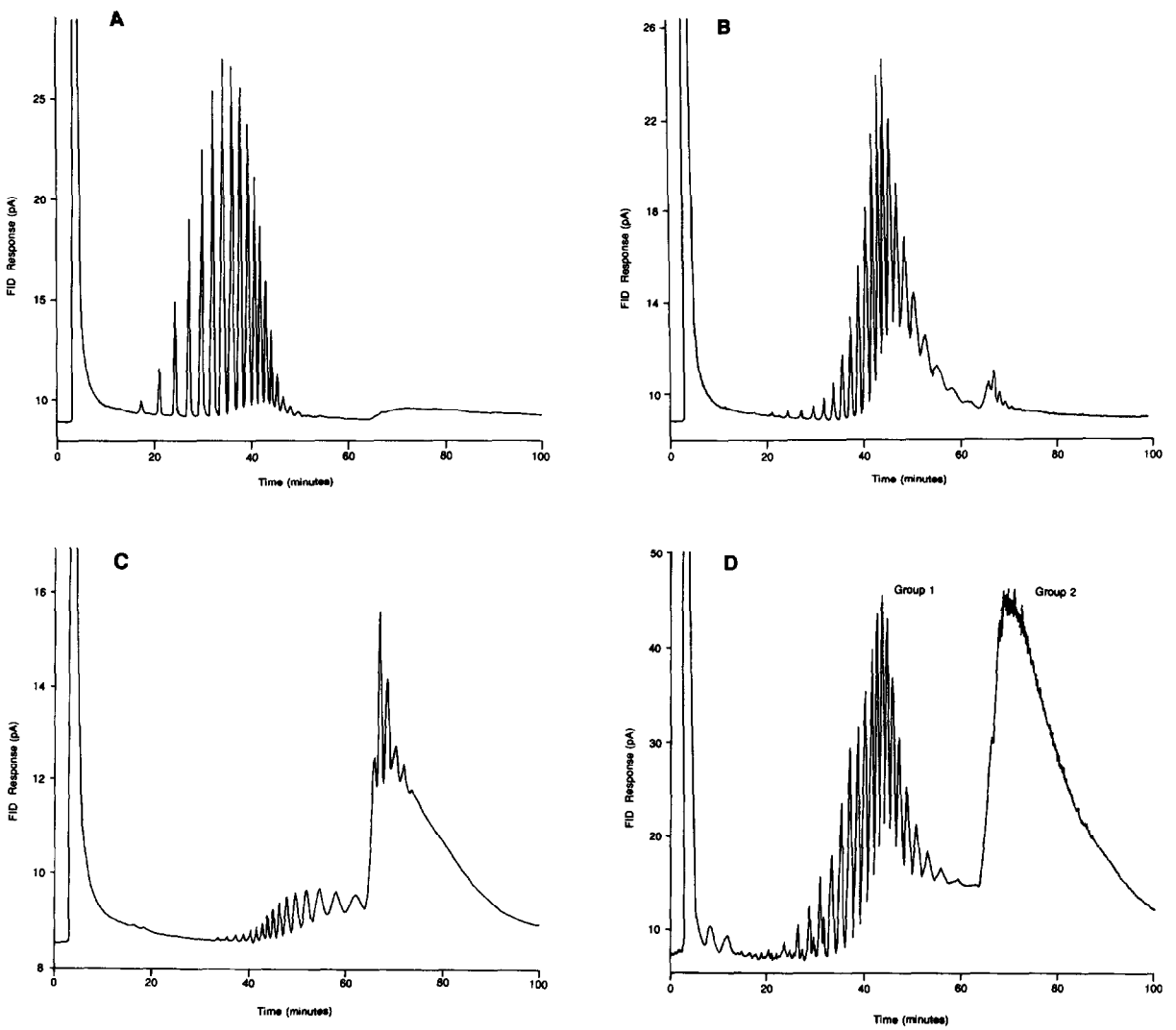

Fig. 4. SFC chromatograms of polyethylene glycol (PEG) and T-MAZ ethoxylated sorbitan fatty acid esters run under the same conditions as in Fig. 2. (A) PEG 600 at concentration, 31.4 mg/ml; (B) PEG 960, 38.0 mg/ml; (C) PEG 1470, 36.5 mg/ml; (D) T-MAZ, 35.4 mg/ml.

high-molecular-mass components in the restrictor [8].

Polyethylene glycol standards

Three PEG standards with molecular masses 600, 960 and 1470, were used to estimate the molecular mass of T-MAZ. Their chromatograms, along with a T-MAZ chromatogram, are shown in Fig. 4A–D. The SFC conditions used in the analysis of PEG standards and T-MAZ were identical. As seen from the chromatograms, SFC demonstrates excellent separation of PEG oligomers in each PEG standard. A total of 18 oligomers were found in PEG 600, 23 in PEG 960, and at least 22 in PEG 1470. With the traditionally used GPC method, only one peak can be seen in each of these PEG standards [9]. Since the molecular mass of each peak in the PEG standards is unknown, it is impossible to make a specific estimation of molecular mass for each peak found in T-MAZ. However, the molecular mass of the oligomers in T-MAZ as groups can be estimated. Assuming that the oligomers of the PEG standards and the oligomers of T-MAZ with the same molecular mass have similar solubility in supercritical carbon dioxide at the same density and have similar interaction with the stationary phase of the capillary column, then the molecular mass of the first group of oligomers in T-MAZ (Fig. 3A) was estimated to be in the range of 900 to 1000, and the second group in the range of 1000 to 1500.

ACKNOWLEDGEMENTS

The authors wish to think Dr. Candida West of US Environmental Protection Agency, Dr. Dennis Fine of ManTech Environmental Technology, Inc., David E. Knowles and Nathen Porter of Dionex Corporation for valuable suggestions and discussions.

DISCLAIMER

Although the research described in this article has beenfunded wholly or in part by the US Environmental Protection Agency through Contract 68-C8-0025 to ManTech Environmental Technology, Inc., it has not been subjected to Agency review and therefore does not necessarily reflect the views of the Agency and no official endorsement should be inferred.

REFERENCES

1 C.C. West and J.H. Harwell, *Environ. Sci. Technol.*, 26 (1992) 2324.
2 M. Harper and C.J. Purnell, *Environ. Sci. Technol.*, 24 (1990) 55.
3 J. Lee, J.R. Crum and S.A. Boyd, *Environ. Sci. Technol.*, 23 (1989) 1365.
4 R. Karrer and H. Herberg, *J. High Resolut. Chromatogr.*, 15 (1992) 585.
5 B.W. Wright, H.T. Kalinoski and R.D. Smith, *Anal. Chem.*, 57 (1985) 2823.
6 R.D. Smith, J.C. Fjeldsted and M.L. Lee, *J. Chromatogr.*, 247 (1982) 231.
7 H.T. Kalinoski, H.R. Udseth, E.K. Chess and R.D. Smith, *J. Chromatogr.*, 394 (1987) 3.
8 D.E. Knowles, L. Nixon, E.R. Campbell, D.W. Later and B.E. Richter, *Fresenius' Z. Anal. Chem.*, 330 (1988) 225.
9 M.Y. Ye, K.D. Hill and R.G. Walkup, *Chromatographia*, in press.