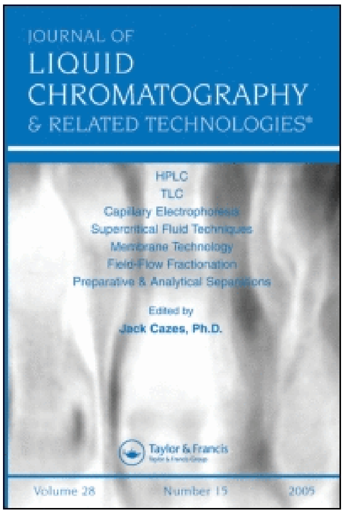

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

Modification of a Gas Chromatograph for Capillary Supercritical Fluid Chromatography

J. L. Hensley[a]; H. M. McNair[a]
[a] Chemistry Department, Virginia Tech, Blacksburg, Virginia

To cite this Article Hensley, J. L. and McNair, H. M.(1986) 'Modification of a Gas Chromatograph for Capillary Supercritical Fluid Chromatography', Journal of Liquid Chromatography & Related Technologies, 9: 9, 1985 — 1996
To link to this Article: DOI: 10.1080/01483918608078756
URL: http://dx.doi.org/10.1080/01483918608078756

JOURNAL OF LIQUID CHROMATOGRAPHY, 9(9), 1985-1996 (1986)

MODIFICATION OF A GAS CHROMATOGRAPH FOR CAPILLARY SUPERCRITICAL FLUID CHROMATOGRAPHY

J. L. Hensley and H. M. McNair
Chemistry Department
Virginia Tech
Blacksburg, Virginia 24061

ABSTRACT

Modification of a gas chromatograph for operation with supercritical fluids can be made in a simple manner without losing the capability for conventional gas chromatography. Using readily available commercial equipment, supercritical fluid chromatography on a level permitting useful application can be performed by many laboratories. A simple analog ramp generator is used to program the pressure of a syringe pump. This work will describe such a system and some of the analytical results obtained.

INTRODUCTION

Supercritical fluid chromatography has received recent attention due to its ability to extend the useful range of capillary chromatographic analysis. The use of a supercritical fluid which combines the solvating power of a conventional liquid with a diffusivity and viscosity similar to a gas allows the analysis of non-volatile, thermally labile compounds (Fig. 1). The use of a supercritical fluid for chromatographic analysis was first described in the literature by Klesper (1) in 1961. This original work utilizing packed columns experienced gradual development during the following years and was developed by Gere et al. (2) using the instrumentation developed for HPLC. Their work led to the development of

0148-3919/86/0909-1985$3.50/0

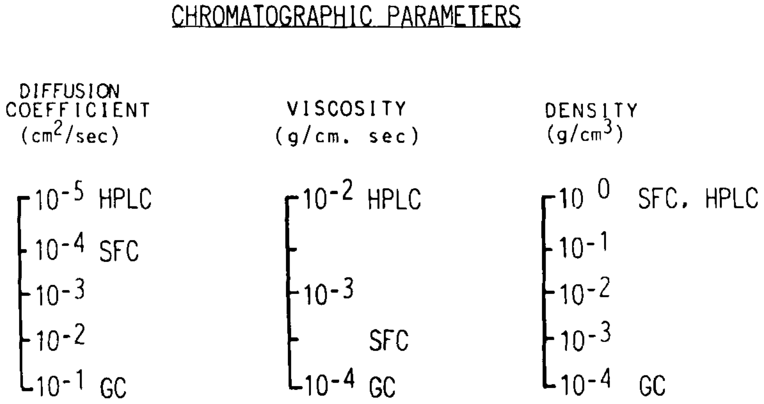

Figure 1. A comparison of the chromatographic parameters of gases, liquids and supercritical fluids.

a commercial packed column SFC instrument and a resurgence of interest in the technique. The logical development of chromatographic analyses toward the use of wall-coated open tubular columns was applied to SFC by Novotny, Lee et al. (3) in the early 1980's. The use of small diameter (100 um i.d.) fused silica capillary columns coated with non-extractable polymeric phases allows the possibility for high efficiency separations (100,000+ theoretical plates) of non-volatile and thermally labile compounds, while the use of smaller (25 um i.d.) columns allows very fast separations to be performed (4).

In order for a chromatographic method to become a useful analytical technique, the method must resolve the peaks of interest from the surrounding matrix in a reproducible manner within a reasonable time frame, while delivering a sufficient amount of material for detection to be made. The use of 100 micron i.d. capillary columns with supercritical fluid CO_2 as a mobile phase has proven satisfactory in meeting these requirements in our laboratory. Our work has utilized commercially available equipment with minimal modification to achieve flame ionization detection with capillary SFC.

Instrumentation

For reference in the following discussion Figure 2 shows a schematic of the SFC chromatograph. The source of CO_2 should be carefully chosen for purity. Initially, we encountered problems with a high background level with some grades and vendors of CO_2. This is to be expected since methane is a known contaminant of CO_2. Since methane, of course, has an appreciable FID response, only the best grades of CO_2 available should be used. The use of scrubber pre-columns has been advocated to remove impurities from the CO_2 but in the case of methane, silica gel and molecular sieve columns have no real utility. Our best results have been obtained by using Coleman Instrument grade CO_2, Matheson (Dorsey, MD) or the new SFC grade CO_2 which has recently been marketed by Scott Specialty Gases (Plumsteadville, PA). The use of a high pressure 2 micron inlet filter inline on the CO_2 delivery line serves to prevent particulate contaminants from reaching the pump.

To satisfy the pumping requirements of capillary SFC the uLC pump from ISCO, (Lincoln, NE) was chosen. In selecting a pump for capillary SFC, pulse free operation is important for the low flow rates (100 to 200 ul/min) used. At the present time this requirement is best met by a syringe type HPLC pump. One advantage of the uLC 500 is its dual mode of delivery by either constant flow or by constant pressure. This ability to provide for solvent delivery by controlling pressure rather than flow rate is extremely advantageous for capillary applications. As an additional aid access ports are provided on the pump controller to provide external control capability of pressure or flow rate. Since the solvent power of a supercritical fluid is proportional to its density which in turn is proportional to its pressure, manipulation of the pressure can affect the analysis in a manner analagous to solvent programming. This control could, of course, be performed by using a microprocessor for a generated pressure profile, but acceptable results can be achieved very economically by a simple analog electronic ramp generator. A ramp generator in combination with the uLC 500 was used by our lab for the applications presented here.

For sample introduction an HPLC submicroliter fixed loop injection valve was used. Two valves were evaluated, the first was a MACS 500 0.5 ul valve from EM Science (Gibbstown, NJ) and the second was a Valco (Houston, TX) 0.1 ul model CI4W. Both valves gave excellent results and were tested with CO_2 at pressures up to 5000 psi without leaks or rotor failure. Following the injection valve an inlet splitter designed for SFC by Scientific Glass and Engineering (Austin, TX) was installed to further reduce the sample size and band width. A Perkin-Elmer (Norwalk, CT) Sigma 2000 gas chromatograph equipped with flame ionization detectors was used for controlling the temperature of the capillary column and for sample detection. The auxillary inlet ports on the side of the instrument provide easy access for the injection valve and inlet splitter while

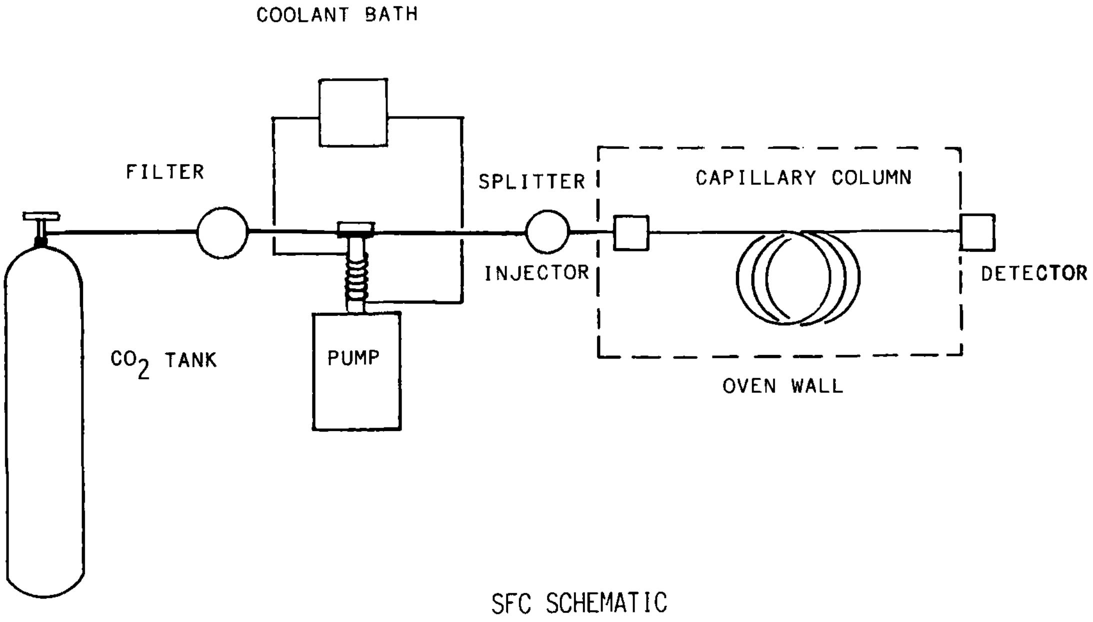

Figure 2. Schematic of a supercritical fluid chromatograph.

allowing the gas chromatographic inlets on the front of the instrument to be retained for use without the necessity for removal of the inlets or for the drilling of holes through the oven wall.

Interfacing the analytical column to the flame ionization detector was accomplished by the use of an SGE glass lined capillary butt connector linking the 100 um analytical column to the 10 um x 4 cm restrictor, which is then fed into the detector in the normal manner. Although reports of spiking and ways to avoid or correct for it have been reported due to the decompression of CO_2 in the FID's (5,6), no spiking was observed with the 10 micron restrictor while spiking was observed with the 5 um restrictor in the pressure region of 3000-5000 psi. For this reason the 10 um restrictor was used for these applications. Data collection was performed by a Perkin-Elmer (Norwalk, CT) LCI-100 integrator and a Perkin-Elmer 3600 Data station.

Applications

The major need for SFC applications is for the analysis of samples not amenable to capillary GC, that is samples that are either non-volatile or thermally labile. The use of fused silica columns minimizes adsorption while the flame ionization detector provides almost universal response for organic compounds. The column used for all the following applications was a 10 meter x 100 um i.d. fused silica column from Polymicro Technologies (Phoenix, AZ) which was coated with OV-1701 after carbowax deactivation and then crosslinked with azo-t-butane according to procedures described earlier (7). Columns prepared in this manner have been extensively used in our laboratory with SFC without phase loss as shown by a reduction in k' values.

A sample of Gulfwax paraffin is shown in Fig. 3. Within 12 minutes the sample has been satisfactory separated at a temperature of 100°C by starting at 2000 psi and pressure programming at 125 psi/min. The temperature used in this example will be used in all succeeding applications since in this region the pressure-density isotherm is nearly linear for CO_2. The surfactant, Triton X-100, has been analyzed extensively by SFC. The separation shown in Fi. 4 is easily made.

A great deal of interest has been generated in SFC due to the techniques ability to handle some polymeric materials. In Fig. 5, a commercial polydimethyl siloxane fluid in methylene chloride is analyzed. A starting pressure of 1000 psi is used to increase resolution in the early part of the sample. Fig. 6 shows another polydimethyl siloxane.

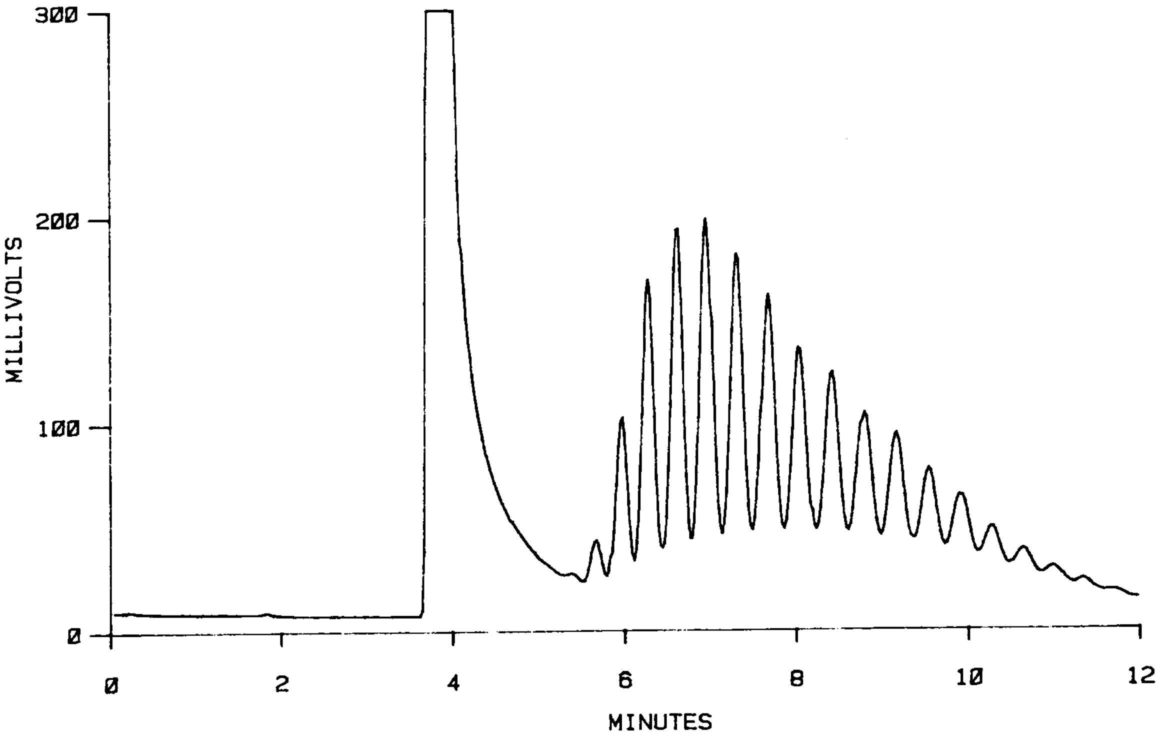

Figure 3. Paraffins from Gulfwax in tetrachloromethane. Initial pressure 2000 psi. Pressure programed at 125 psi/min. Column temperature 100°C.

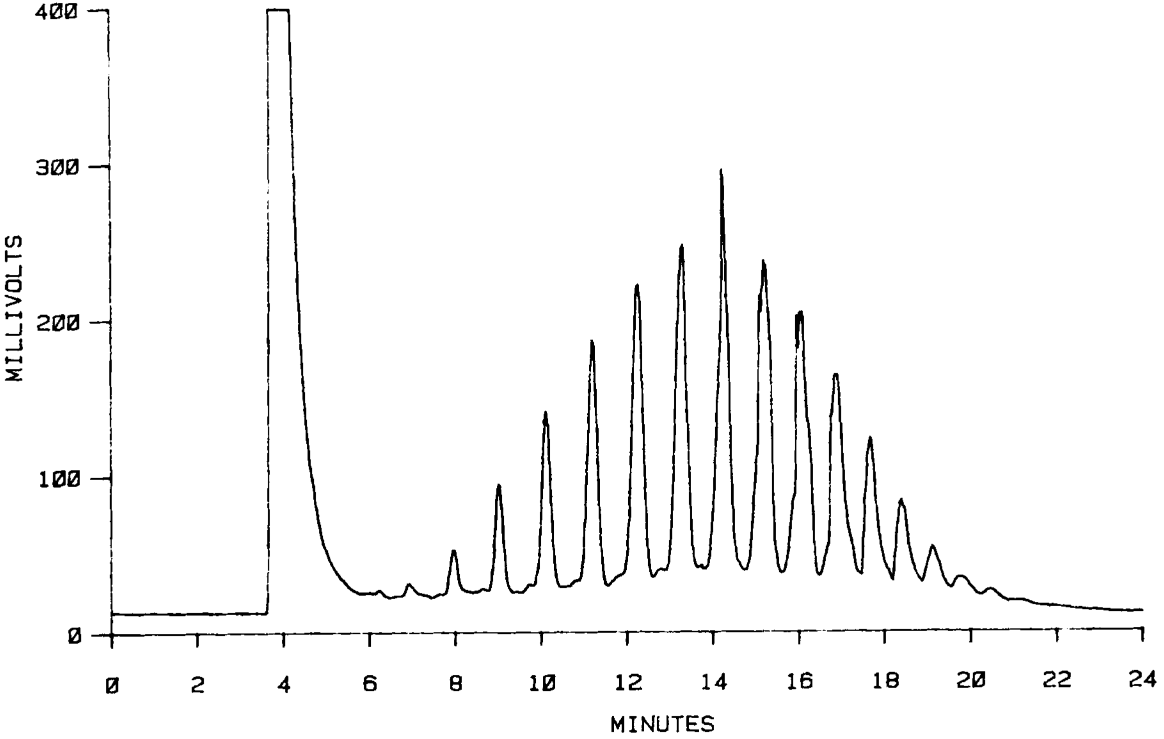

Figure 4. Triton X-100 in 80/20 methanol/water. Initial pressure 2000 psi. Pressure programed at 125 psi/min. Column temperature 100°C.

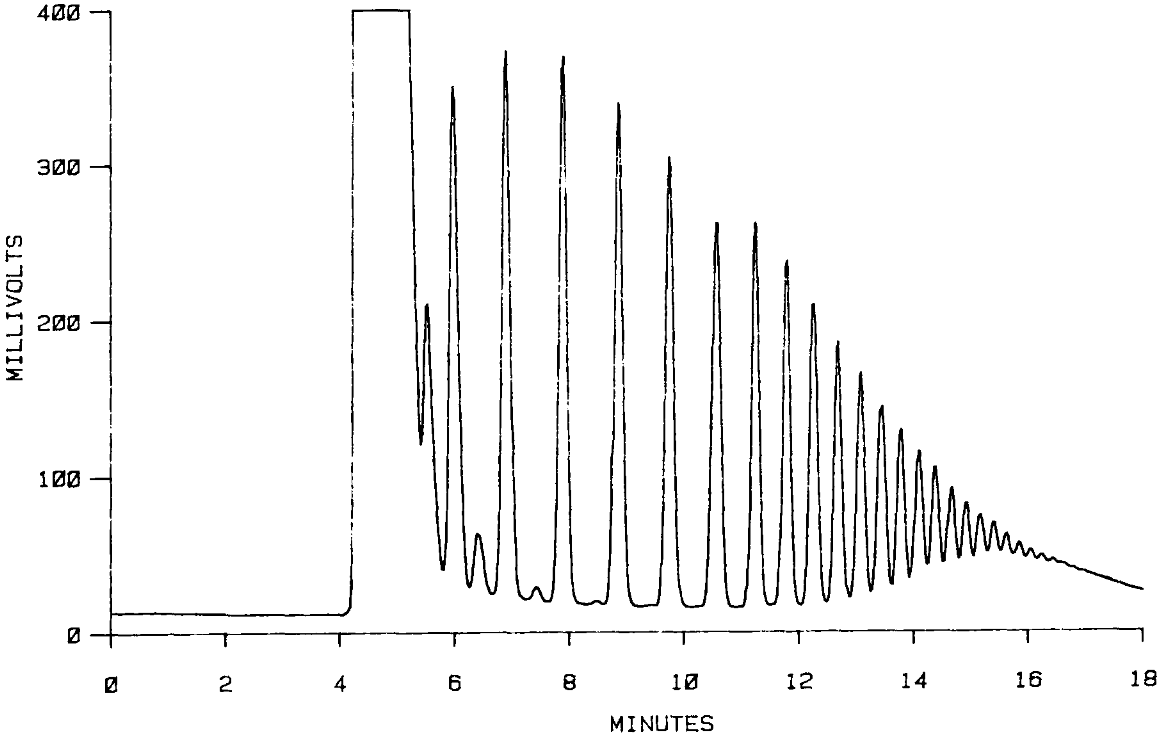

Figure 5. Commercial polydimethyl siloxane fluid in dichloromethane. Initial pressure 1000 psi. Pressure programed at 125 psi/min. Column temperature 100°C.

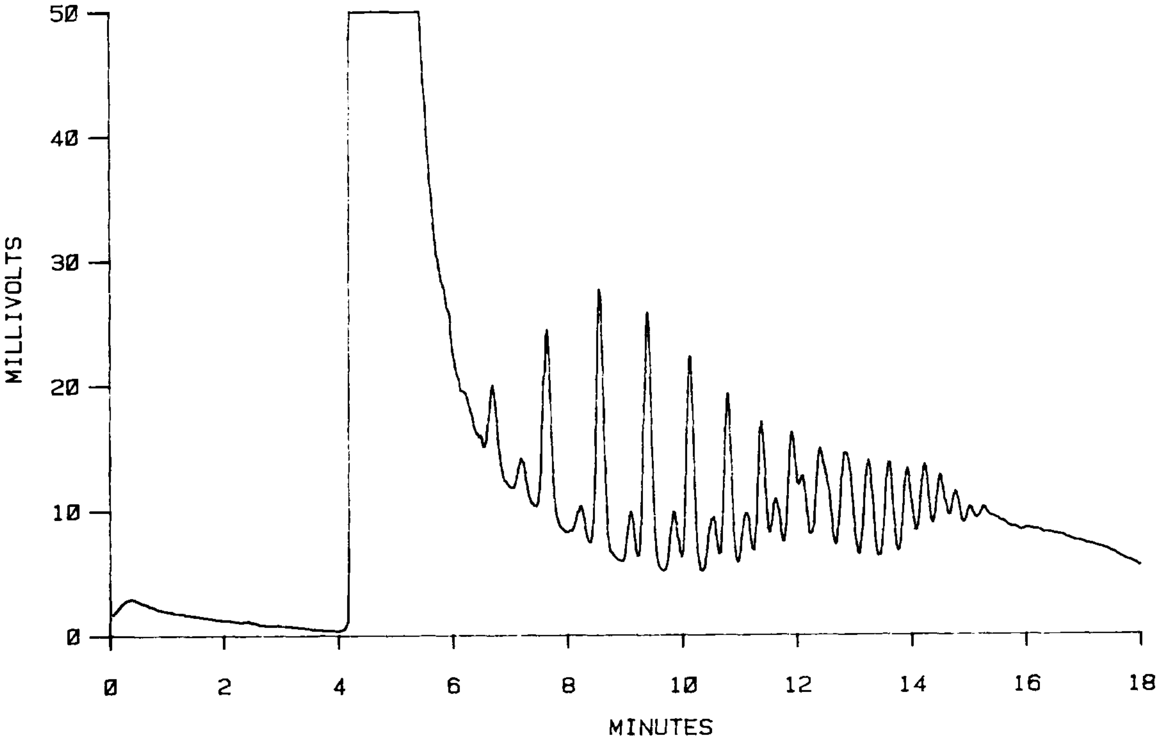

Figure 6. SF-96 polydimethyl siloxane fluid in dichloromethane. Initial pressure 1000 psi. Pressure programed 125 psi/min. Column temperature 100°C.

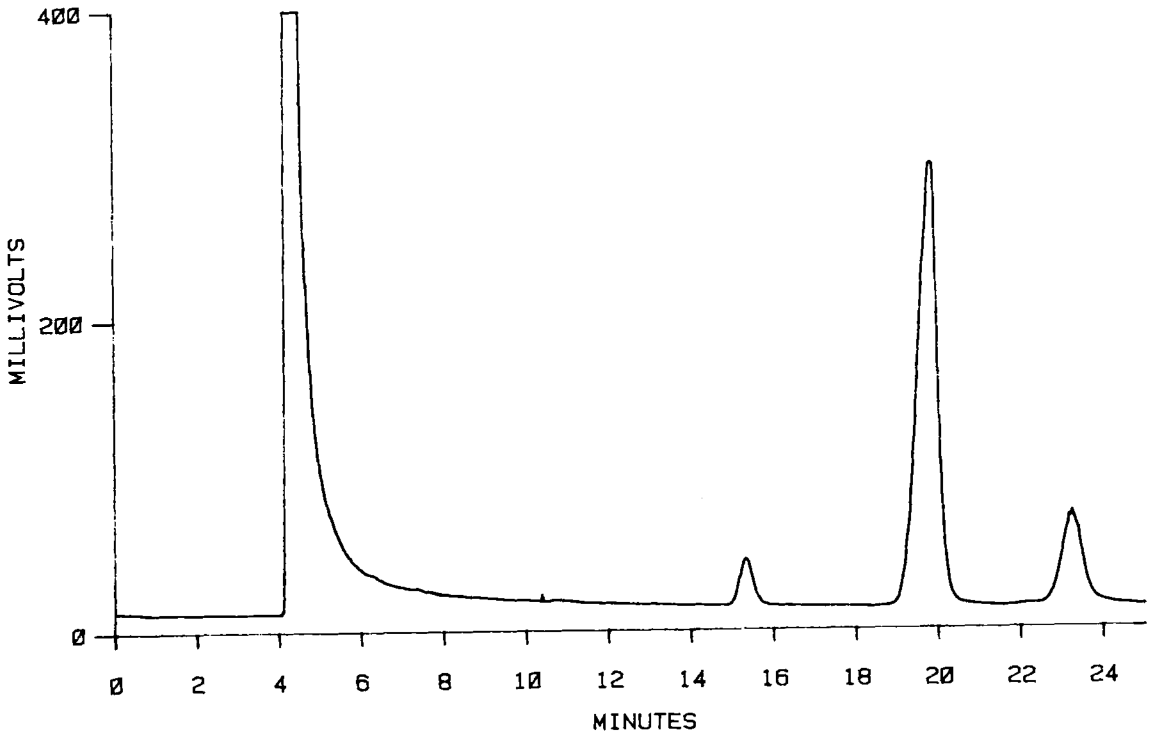

Figure 7. OV-235 poly cyano methyl phenyl siloxane gum in dichloromethane. Initial pressure 2000 psi. Pressure programed at 125 psi/min. Final pressure 5000 psi. Hold 1 minute. Column temperature 100°C.

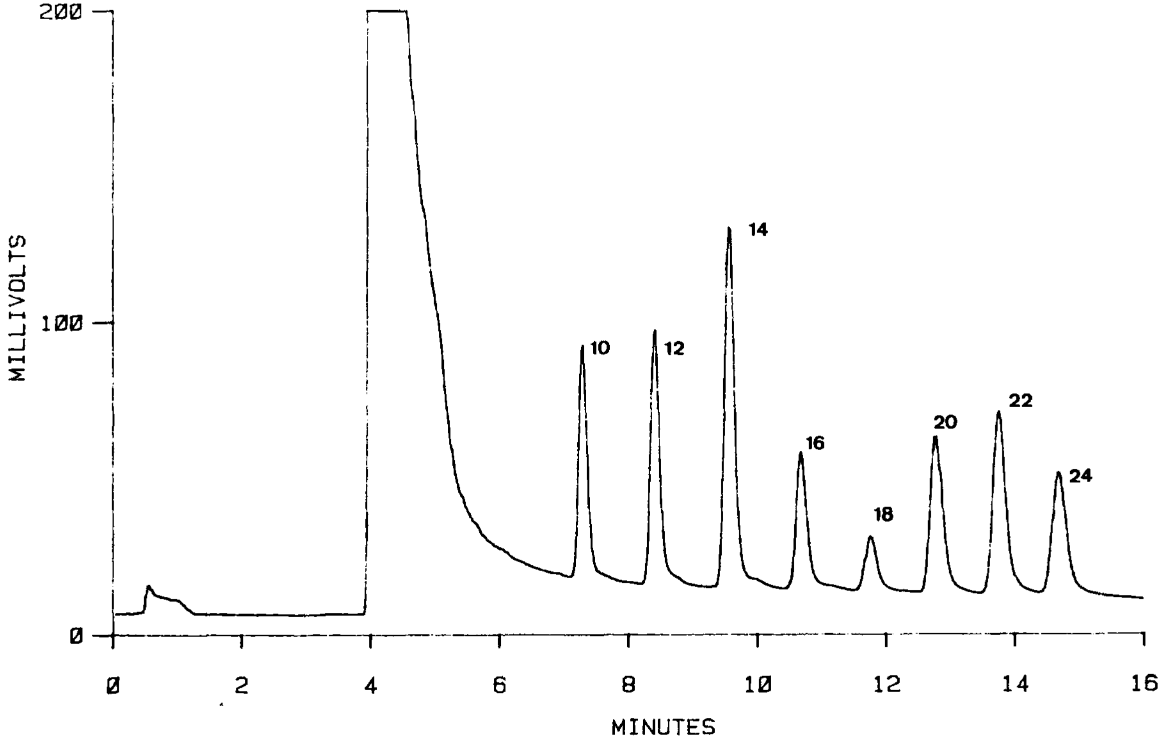

Figure 8. Fatty acids in dichloromethane (C 10 - C 24). Initial pressure 1500 psi. Pressure programed at 125 psi/min. Column temperature 100°C.

In this case the sample is a gas chromatographic stationary phase, SF-96. The last chromatogram, another gas chromatographic stationary phase, OV-235, is shown in Fig. 7. This phase is a vinyl modified version of OV-225, a 50% phenyl-methyl, 50% cyanopropylmethyl polysiloxane. Fig. 8 shows a separation of fatty acids with carbon numbers of C 10-C 24. In this case, the sample was analyzed at 100°C with the last peak out in 15 minutes.

CONCLUSION

The instrumentation needed to perform SFC is not exotic or unique to these applications. Many laboratoris can perform useful analyses using supercritical fluid chromatography with a minimum expenditure for additional equipment. Fused silica capillary columns provide the potential for a major improvement in resolution over packed SFC columns and the FID gives a universal means of detection for organic compounds with an easily calibrated response.

Acknowledgement: This work was funded by a grant from Combustion Engineering of Lewisburg, West Virginia. Their support is greatly appreciated.

REFERENCES

1. Kesper, E., Corwin, A.H., and Turner, D.A., J. Org. Chem., 27, 700, 1962.

2. Gere, D., Science, 222, 253, 1983.

3. Novotny, M, Springston, S.F., Peaden, P.A., Fjeldsted, J.C. and Lee, M.L., Anal. Chem., 53, 407A, 1981.

4. Wright, B.W. and Smith, R.D., HRC&CC, 8, 8, 1985.

5. Richter, B,E., HRC&CC, 8, 297, 1985.

6. Fjeldsted, J., Kong, R.C. and Lee, M.L., J. Chrom., 279, 449, 1983.

7. Ogden, M.W. and McNair, H.M., HRC&CC, 8, 326, 1985.