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DEVELOPMENT OF SUPERCRITICAL FLUID CHROMATOGRAPHY FOR ANALYSIS OF TRUEX PROCESS SOLVENTS

by

P.-K. Tse and G. F. Vandegrift

Chemical Technology Division

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TABLE OF CONTENTS

TABLE OF CONTENTS (contd)

LIST OF FIGURES

LIST OF FIGURES (contd)

LIST OF TABLES

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ABSTRACT

This report summarizes the work that has been performed at Argonne National Laboratory on the development of an analytical procedure to analyze TRUEX process solvents; these solvents are composed of a bifunctional organophosphorus extractant(octylphenyl-N,N-diisobutylcarbamoylmethylphosphine oxide,OØD[iB]CMPO or simply CMPO) and tributylphosphate (TBP) in either a normal paraffinic hydrocarbon (NPH) or tetrachloroethylene (TCE) diluent. Supercritical fluid chromatography (SFC) was chosen for this analytical technique because it yields a good separation of the components of the TRUEX solvent and is useful at temperatures below the decomposition temperature of CMPO (~180°C). Discussed are concepts important to using SFC for chromatographical separations and with four different detectors: flame ionization detector (FID), nitrogen/phosphorus detector (NPD), mass spectrometer (MS), and ultraviolet (UV) detector. A comparison of the four detectors for the analysis of CMPO, TBP, and the TRUEX solvents shows that FID is the best for quantitating CMPO, TBP, and the degradation products. The mass spectrometer is the best for identifying unknown impurities and degradation products. Standard procedures based on the results of this study are reported for analysis of CMPO alone, CMPO dissolved in TBP, and the TRUEX-NPH and TRUEX-TCE solvents.

I. INTRODUCTION

The TRUEX process is a solvent extraction procedure capable of separating, with very high efficiency, small quantities of transuranic (TRU) elements (e.g., Np, Am, Pu, and Cm) from aqueous nitrate or chloride solutions that are typically generated in fuel reprocessing and plutonium production and purification operations. The ability of the TRUEX process to remove, separate, and recover TRU elements from aqueous media with a wide range of compositions gives it the potential for treating the entire range of TRU and high-level waste streams generated at DOE facilities. The application of a TRUEX process at these facilities would produce three important results: (1) alleviate both long- and short-term waste storage problems that threaten to curtail production; (2) reduce the volume of TRU waste generated by a processing plant by two orders of magnitude--the bulk of the waste being nonTRU and a candidate for near-surface disposal; and (3) recover plutonium that would otherwise be lost to waste disposal.

The key ingredient in the TRUEX solvent extraction process is octyl (phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide, which is generally called CMPO. This extractant is combined with tributyl phosphate (TBP) in a diluent to formulate the TRUEX solvent. The diluent is typically a normal paraffinic hydrocarbon (NPH) or a nonflammable chlorocarbon such as tetrachloroethylene (TCE). The composition of the TRUEX solvent is dependent on the diluent of choice. The TRUEX-NPH solvent is composed of 0.2M CMPO, 1.4M TBP, and Conoco C_{12}-C_{14} NPH as the diluent; the TRUEX-TCE solvent is composed of 0.25M CMPO, 0.75M TBP, and TCE as the diluent.

The goal of the TRUEX Technology-Base Development Program, currently underway in the Chemical Technology Division of Argonne National Laboratory, is to facilitate the implementation of TRUEX processing in the DOE community wherever it can be of financial and operational advantage. This report discusses one aspect of the program goals, the development of a reliable analytical tool for (1) measuring the purity of the commercially available CMPO that is to be used in TRUEX processing and (2) monitoring the TRUEX solvent composition in plant situations.

Because the extraction and stripping of many metal ion salts (e.g., Am and rare earth fission products) depend on the concentration of CMPO to the third power, small differences in CMPO concentration can greatly affect the efficiency of a multi-stage, countercurrent TRUEX process flowsheet. For example, if the CMPO concentration were 10% below its expected value, the distribution ratio (D) would be reduced to $(0.9)^3 = 73\%$ of its expected value. For a six-stage extraction section, where the value of D is expected to be 8 but, because of the lower [CMPO], is only 5.8, the concentration of americium in the raffinate would be $(1/5.8)^6 = 2.5 \times 10^{-5}$ of its original feed concentration. If the concentration of CMPO were correct, the reduction should have been $(1/8)^6 = 3.8 \times 10^{-6}$; i.e., the Am concentration in the raffinate would be almost seven times higher than expected. In this example, the purpose of running the TRUEX process, i.e., to make the raffinate a nonTRU waste (<100 nCi/g), would be in great jeopardy due to the 10% lower concentration of CMPO in the solvent.

The analytical technique which we have chosen to develop for CMPO and TRUEX solvent analyses is supercritical fluid chromatography (SFC). The reasons for this decision are:

- It is a low temperature technique that can accurately measure CMPO without decomposing it, thus giving spurious results. CMPO begins to decompose at ~180°C; SFC analyses are performed at <120°C.

- It has the ability to be used with all the detectors that are presently available for gas chromatography (GC), including highly sensitive and efficient flame ionization detectors (FID) and mass spectrometers (MS).

- The SFC analyses are run much like GC and high performance (or pressure) liquid chromatography (HPLC) and can be easily automated to increase productivity and improve quality control.

This report describes the fundamentals of SFC and the results of our development of SFC for use in TRUEX-processing facilities. Appendixes A-E describe standard analytical procedures for the TRUEX-TCE and TRUEX-NPH solvents, CMPO, and CMPO dissolved in TBP.

II. SUMMARY AND CONCLUSIONS

The goal of this study was to test the applicability of SFC to quantitating (1) the purity of commercially available CMPO and (2) the compositions of the TRUEX-TCE and TRUEX-NPH solvents under plant conditions. Although actual in-plant use has not been established, results obtained in this laboratory show that the SFC technique should be useful in this situation.

Supercritical fluid chromatography has been demonstrated to be a very useful technique to analyze thermally unstable compounds such as CMPO. Under the operating conditions chosen for analysis of CMPO and the TRUEX-NPH and TRUEX-TCE solvents, no decomposed CMPO will be detected in the injection valve or in the column. The CMPO and TBP are well separated from each other and from their impurities and the TCE and NPH diluents. The separation factor between CMPO and TBP is greater than 10. The reproducibility between duplicate samples is <0.1% for retention times and 2% for peak areas. Running replicate samples for each analysis and using an internal standard can decrease the errors in peak-area measurements even further.

The SFC technique allows wide flexibility in optimization of chromatographic conditions for the analysis. In an SFC system, analysis temperature, mobile-phase composition, mobile-phase density, stationary-phase composition, column dimensions, and specific detectors are parameters that can be varied to meet the desired analysis criteria. This report demonstrates that the efficiency of chromatographic separation of TRUEX solvent components and their impurities and degradation products is affected by several of these factors. The optimum conditions for analysis of CMPO and the TRUEX-NPH and TRUEX-TCE solvents are described in Appendixes A-D. A method for quantitatively standardizing the system using an internal standard is described in Appendix E.

III. DESCRIPTION OF SUPERCRITICAL FLUID CHROMATOGRAPHY

Supercritical fluid chromatography is a chromatographic technique that shares many properties with the well-known techniques of GC and HPLC [AHUJA-A, AHUJA-B, CHARPENTIER, LEE-B].

Due to the high diffusivities and low viscosities in a gas mobile phase, the separating capability of GC is unparalleled with respect to all the other chromatographic methods. Its compatibility with a wide variety of sensitive and selective detectors makes GC the choice of chromatographic methods if it can be applied to the sample of interest. However, this method is restricted by the limited volatility and thermal stability of many compounds of interest.

Mixtures of less volatile compounds can be analyzed by HPLC. In HPLC, the separation of compounds relies on partitioning of species between the carrier liquid and the stationary phase and is achieved by the variation of both mobile phase and stationary phase compositions to achieve variations in interaction with solutes.

In SFC, the mobile phase is a dense gas with appreciable solvating strength to solute molecules of interest. Figure 1 shows the ranges of temperature and pressure for a supercritical fluid. Above the critical temperature, the supercritical fluid cannot be liquefied by increasing the pressure. The definition of a supercritical fluid is arbitrary, in that there is a continuous transition (1) from liquid to supercritical fluid by increasing the temperature at constant pressure or (2) from gas to supercritical fluid by increasing the pressure at constant temperature. The properties of supercritical fluids fall between those of gases and liquids, as shown in Table 1 [LEE-A].

By controlling the temperature and/or pressure of a supercritical fluid (varying its density), the solvating character of a supercritical fluid can be varied. The densities of typical supercritical fluids are 0.2-0.9 g/mL. Table 1 shows that the diffusion coefficients of supercritical fluids are substantially greater than those of liquids but smaller than those of gases. Similarly, the viscosity of supercritical fluids is lower than that of liquids, but higher than that of gases. The density of the supercritical fluid will normally be 100 times greater than that of its gaseous state at ambient pressures. Because of short intermolecular distances, the interaction between molecules increases. The "liquid-like" density of supercritical fluids enhances their solvating power compared to the gaseous state. The lower viscosities and higher diffusion coefficients in supercritical fluids relative to liquids result in significantly enhanced chromatographic efficiency compared to HPLC.

The application of SFC to a specific analysis is determined by the solvating power of the supercritical fluid. Solutes are generally characterized by a pressure above which solubility increases significantly; the region of maximum increase in solubility as a function of pressure is near the critical pressure, where the change in density with pressure is greatest. A linear relationship between log[solubility] and density for dilute solutions of a nonvolatile compound in a supercritical fluid has been observed [SMITH]. When the solute volatility is extremely low and its density is less than (or near)

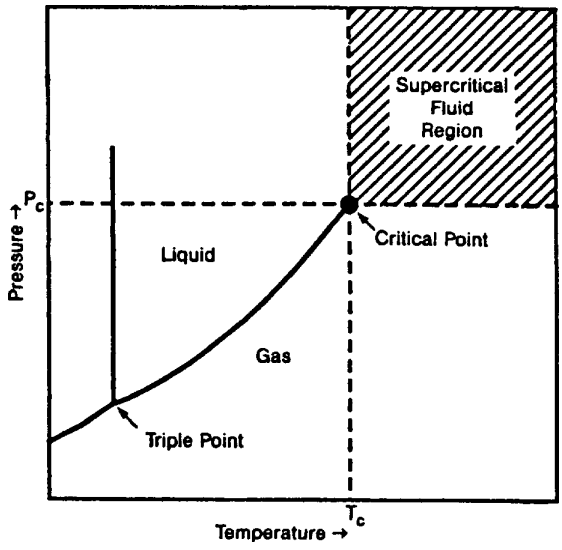


Fig. 1.

Pressure-Temperature Diagram for a Pure Component

Table 1. Typical Properties of Mobile Phases Used in Chromatography

Mobile Phase	Density, g/mL	Viscosity, poise x 10^{-4}	Diffusion Coefficient, cm^2/s
Gas	(0.6-2.0) x 10^{-3}	0.5-3.5	0.01-1.0
Supercritical Fluid	0.2-0.9	2.0-9.9	(0.5-3.3) x 10^{-4}
Liquid	0.8-1.0	30-240	(0.5-2.0) x 10^{-5}

the critical density, increasing temperature will decrease solubility. However, the solubility of the solute may increase at high temperatures, where the solute vapor pressure can also become significant.

For volatile solutes, the solute vapor pressure can also produce a significant effect. Under conditions of constant density, their solubilities generally increase with temperature.

The highest supercritical fluid densities at a given pressure are obtained near the critical temperature. The greatest solubilities (at given pressure limitation) and more-rapid chromatographic elution will often be obtained at somewhat lower densities but higher temperatures.

IV. BACKGROUND

A. Theory of Chromatographical Separations

The following discussion is presented to familiarize the reader with the concepts and terms important to discuss a chromatographic technique. This discussion summarizes concepts presented by several authors [PEADEN-B, RANDALL, NOVOTNY, WASEN].

1. Resolution

The purpose of any chromatographic system is to separate compounds from each other and identify and/or quantitate them. Like other chromatographic techniques, SFC depends on the resolution between components. The most fundamental equation expressing resolution (R) between two components (peaks) is:

$$R = \frac{1}{4} \cdot \frac{\alpha - 1}{\alpha} \cdot \frac{k'}{1 + k'} \cdot N^{1/2} \qquad (1)$$

where k' = capacity factor for the second peak to emerge, α = selectivity, and N = column efficiency or number of theoretical plates. The capacity factor k' is defined as

$$k' = \frac{t_r - t_o}{t_o} \qquad (2)$$

where t_r is the elution time of a compound of interest, and t_o is the elution time of a theoretically unretained substance. Capacity factors are measures of the partitioning of a component between the stationary and mobile phases and are defined as the ratio of the mass of a component in the stationary phase over that in the mobile phase. The selectivity α is defined in terms of the ratio of the capacity factors of the two components:

$$\alpha = \frac{k_2'}{k_1}, \geq 1 \qquad (3)$$

The number of N is given by the column length (L) divided by the height of a theoretical plate (H):

$$N = \frac{L}{H} \qquad (4)$$

The second term on the right-hand side in Eq. 1, $(\alpha - 1)/\alpha$, requires that α be significantly different from 1 for a significant resolution of the two peaks. This must be achieved by proper choice of mobile fluid and stationary phase; otherwise, no resolution is obtainable, even with a large number of theoretical plates.

The third term, $k'/(1 + k')$, is significant in the range $0 < k' < 20$. If $k' = 0$, R will always equal zero. Even at $k' = 9$, very little can be gained in terms of resolution by increasing the k' value further. Moreover, higher k' values imply longer analysis times (Eq. 2).

Again, according to Eq. 1, R is directly proportional to the square root of column efficiency, N. If all other chromatographic conditions remain constant, N will be proportional to the column length (Eq. 4 with H constant), and the analysis time for component i ($t_{r,i}$) will be expressed as

$$t_{r,i} = \frac{L}{v_i} \tag{5}$$

where v_i is the average linear flow velocity of the solute molecular zone, i. Resolution can be increased by a factor of two at the expense of an increase by a factor of four in the column length and, therefore, in analysis time. However, increasing the column length to increase N will lead to an increased pressure drop over the column. If the pressure drop becomes too high, parameters other than the column length will have to be varied. Increasing N may, therefore, be an unrewarding factor for increasing the resolution.

2. Peak Broadening

The number of theoretical plates in a SFC column is inversely proportional to the theoretical plate height, H (Eq. 4). Peak-broadening mechanisms are more easily discussed in terms of H.

For a column defined as a smooth-wall, open tube coated with a stationary phase of a uniform film of thickness d_f, the expression for H is [GOLAY]:

$$H = \frac{2D_m}{v} + \frac{(1 + 6k' + 11k'^2)d_c^2 v}{96(1 + k')^2 D_m} + \frac{2k' d_f^2 v}{3(1 + k')^2 D_s} \tag{6}$$

where D_m = Diffusion coefficient of the solute in the mobile phase
D_s = Diffusion coefficient of the solute in the stationary phase
v = Mobile phase average linear flow velocity
d_c = Column diameter
d_f = Stationary phase film thickness

For packed columns, H is expressed as [KARGER]:

$$H = 2\lambda d_p + \frac{2\gamma D_m}{\bar{v}} + \frac{2\,k'}{(1 + k')^2}\, t_s + \frac{\omega d_p^2}{D_m}\,\bar{v} \qquad (7)$$

where λ = Packing correction factor
d_p = Particle diameter
γ = Tortuosity factor
D_m = Solute diffusion coefficient in the mobile phase
t_s = Mean residence time of the solute molecule in the stationary phase
ω = A flow-path-dependent term
$\bar{v}$ = Average linear flow velocity

Generally, H may be expressed in the form of the van Deemter equation [GERE]:

$$H = A + \frac{B}{\bar{v}} + C\bar{v} \qquad (8)$$

The first term on the right-hand side in Eq. 7 (or Eq. 8) accounts for the longitudinal convective mixing as a cause of peak broadening. This mixing is due to the interstitial flow pattern of the mobile phase and is velocity independent. The second term describes the longitudinal diffusion as a cause of peak broadening. Since the relative magnitude of D_m is small and $\bar{v}$ is usually relatively large, the second term can probably be neglected in many cases. The last term, c, consists of two additive components. The first component accounts for nonequilibrium in radial transport of the substrate between mobile and stationary phases. It becomes small when k′ is large and when t_s is small (i.e., when there is a high rate of solute transfer to and from the stationary phase). A pressure as small as possible, a temperature as high as possible, and a layer of stationary liquid on the carrier particle as thin as possible are of advantage to realizing this condition. The second component of C may be looked upon as due to the hindered diffusive and convective radial transport of the substrate in the mobile phase between the different velocity regimes associated with the interstitial flow pattern. A small particle size, higher temperature, and, probably, turbulent flow are of advantage to minimizing this component. Also, because they will lead to a decrease in t_s and ω, high diffusion coefficients and low viscosities are important to minimize both components of this term.

3. Analysis Time

The relative speed of analysis of packed vs. capillary columns in SFC may be compared by means of the parameter H_{min}/v_{opt} [RANDALL] where the minimum plate height, H_{min}, is expressed for a packed column in terms of:

$$H_{min} = 2d_p \left[\lambda + \frac{(1 + k' + 11\,k'^2)^{1/2}}{2\sqrt{3}\,(1 + k')} \right] \qquad (9)$$

The optimum linear velocity, v_{opt}, is expressed for a packed column in terms of:

$$v_{opt} = \frac{4\sqrt{3}\ D_m(1 + k')}{d_p\ (1 + 6\ k' + 11\ k'^2)^{1/2}} \tag{10}$$

For capillary columns, the internal diameter of the column (d_c) replaces the particle diameter (d_p) in Eqs. 9 and 10. Based on experimental results, Peaden and Lee showed that for $1 < k' < 5$, the ratio H_{min}/v_{opt} for packed and capillary columns can be compared through the relationships [PEADEN-A]:

$$\frac{H_{min}}{v_{opt}} = \frac{2}{3}\frac{d_p^2}{D_m} \quad \text{for packed columns} \tag{11}$$

$$\frac{H_{min}}{v_{opt}} = 0.1\frac{d_c^2}{D_m} \quad \text{for capillary columns} \tag{12}$$

For equal speeds of analysis in a packed capillary column, d_c would need to be equal to 2.6 d_p. For a given separation, therefore, a 50 μm ID capillary column corresponds to a column packed with 20 μm particles.

4. Number of Theoretical Plates vs. Column Type

The smaller pressure drop across the capillary column allows longer columns with larger numbers of plates. For equal pressure drops

$$\frac{\eta_c}{\eta_p} = 4.6\ \left(\frac{d_c}{d_p}\right) \tag{13}$$

where η_c and η_p are the maximum number of theoretical plates on capillary and packed columns, respectively [SCHOENMAKERS].

5. Effects of Pressure Changes on SFC Separations

In SFC, pressure (p) plays a very important role, having a direct effect on retention, selectivity, and diffusion rates. All these parameters have an important relationship to the resolving power of a chromatographic system. All the effects of column pressure can be related to the density (ρ) of the mobile phase. If the pressure change is very small, the relationship between changes in density and pressure is

$$\frac{\Delta\rho}{\rho} = S\frac{\Delta p}{p} \tag{14}$$

[PEADEN-B]. Under normal SFC conditions, S (the fractional density change per change in pressure) varies from 0.2 to 6.

The effects of mobile phase density on the capacity factor (k'), and therefore retention time (Eq. 2), can be described by the following equation:

$$\log k' = a - b\rho \tag{15}$$

where a and b are factors that are dependent on the types of compounds being separated, the nature and temperature of the mobile phase, and the nature of the stationary phase [PEADEN-C].

The density of the mobile phase also affects the selectivity ($\alpha = k_2'/k_1'$) as shown in the following equation:

$$\log\alpha = B_o - m\rho \tag{16}$$

where B_o and m are also system-dependent constants.

Diffusion in the mobile phase depends on both the density and viscosity of the mobile phase.

B. Detectors

1. General Requirements for Widely Useful Detector

To be useful for supercritical fluid chromatography, a detector must have adequate

- sensitivity for most substances (unless selectivity for one compound or group of compounds is desired),
- stability, and
- linear dynamic range.

The definitions of these characteristics are given below.

a. Sensitivity

Detector sensitivity, S, is defined as the detector response to the change of detected quantity of the compound of interest in the carrier. Therefore, the sensitivity can be expressed for a mass-flow-rate dependent detector as

$$S = \frac{A}{M} \tag{17}$$

where A is the integrated peak area, and M is the sample mass. For concentration-dependent detectors, the response is proportional to the concentration of the sample in the carrier and is defined as:

$$S = \frac{h_t}{C} \tag{18}$$

where h_t is the peak height, and C is the concentration.

b. Stability

Stability means that the detector will produce a stable and narrow baseline when operated at its highest sensitivity. For a given detector, optimum baseline stability is obtained by using high purity carrier gases and maintaining constant gas flow rates and detector temperatures.

c. Linear Dynamic Range

The linear dynamic range is defined as the incremental change in sample size that produces an incremental change in detector response to within ± 5% of linearity.

2. Specific Detectors

Although dozens of different detectors have been coupled to SFC and examined by chromatographers, only four of the most highly developed detectors will be considered here.

a. Flame Ionization Detector (FID)

The flame ionization detector is the most commonly used detector in SFC. The properties that make it the best choice for most applications are:

- It is the most insensitive detector to fluctuations in operating variables.
- It is highly sensitive to organic carbon-containing compounds.
- It is relatively insensitive to small changes in column flow rate.
- It has vanishingly low noise levels.
- It has an extremely wide linear dynamic range (10^7).

The limitations of FID are:

- It has little or no response to compounds such as N_2, O_2, CO, CO_2, H_2O, H_2S, CS_2, COS, HCN, NH_3, NO, N_2O, N_2O_3, CCl_4, SCl_4, CH_3SiCl_3, SiF_4, and all noble gases.

- It is a destructive detector.
- Its response is strongly dependent on the structure of the sample and on the presence of heteroatoms (e.g., the presence of O, S, and halogens decreases the response of the FID).
- Chlorinated solvents such as CH_2Cl_2 and $CHCl_3$ produce soot and black smoke in the hydrogen-rich flame, which cause detector instability. (A hotter flame with lower hydrogen content can prevent this incomplete combustion of chlorinated solvents.)

A schematic diagram of the FID is shown in Fig. 2 [LEE-C]. The restrictor interfaces to the detector via a connector union and vespel ferrule. The make-up gas (N_2) at the connector is used for minimizing both band broadening from the connector volume and the detector cell volume and for preventing back diffusion of sample into the interface. Make-up gas is also required to optimize the detector response and stability. An air-to-hydrogen fuel gas ratio of approximately 10 was demonstrated to give good flame stability and ionization efficiency [CONDON].

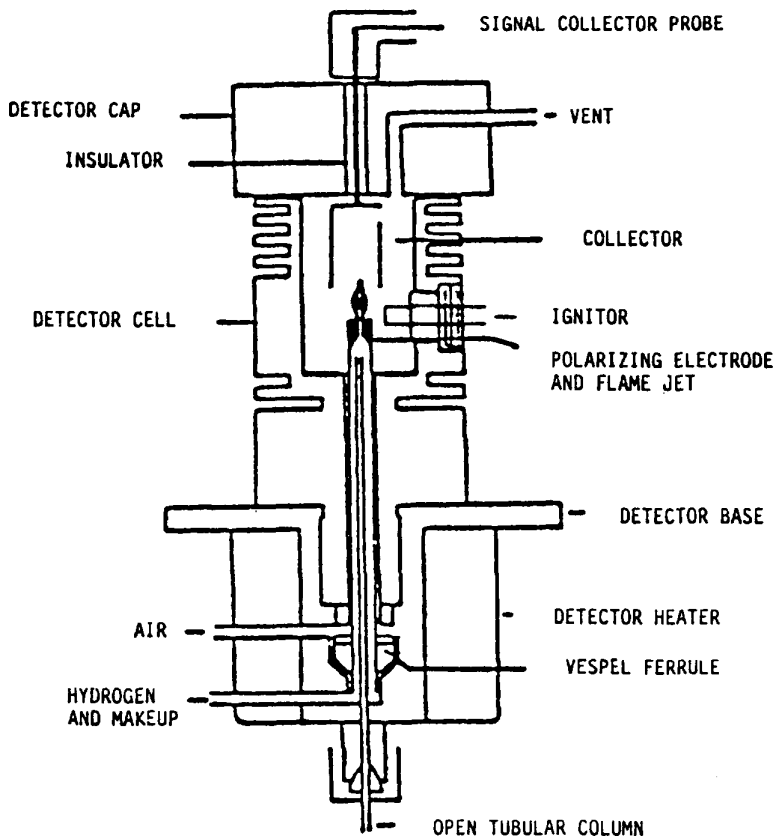


Fig. 2. Diagram of a Flame Ionization Detector. (Reprinted with permission from [LEE-C].)

b. Thermionic Nitrogen/Phosphorus Detector

The nitrogen/phosphorus detector (NPD), one type of a thermionic specific detector (TSD), is also a destructive and mass-flow-rate dependent detector. The basic design of the NPD is quite similar to the FID, except that alkali-metal-salt beads are situated between the burner tip and the collector (Fig. 3). Electrically heated alkali metal ions (Na, Rb, or Cs) are contained in a matrix of silica or ceramic beads, which, in turn, coat the coiled heater probe [KOLB, LUBKOWITZ]. Bead temperature is controlled by the input current. The temperature of the alkali source determines the vapor pressure and the thermal energy of the alkali metal and affects the sensitivity, background current, and lifetime of the detector.

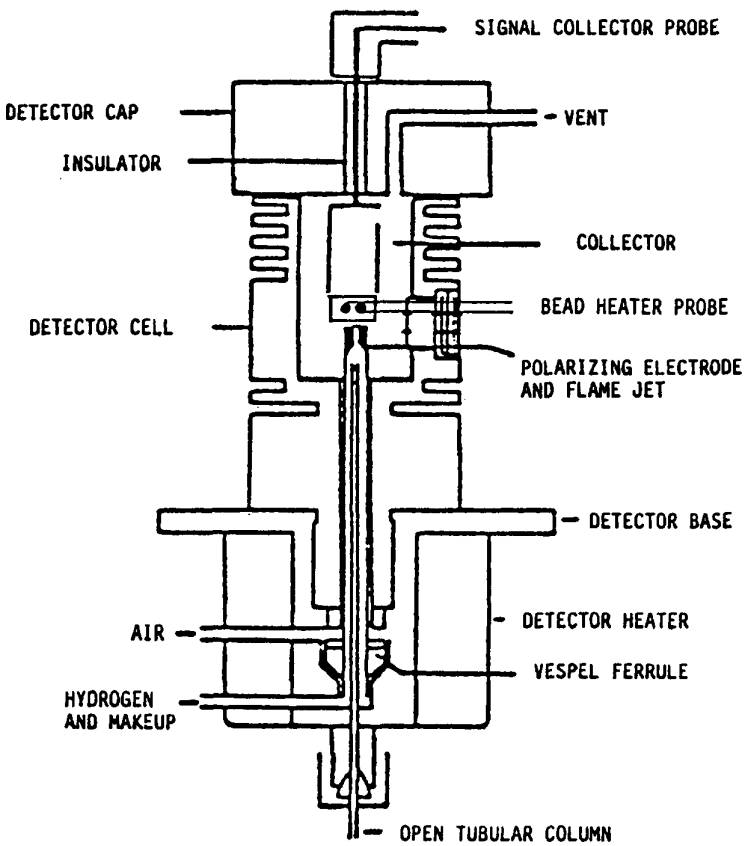


Fig. 3. Diagram of a Nitrogen-Phosphorus Detector. (Adapted from [LEE-C].)

Several models have been proposed to account for the selectivity of the TSD response to nitrogen and phosphorus. They differ principally in whether the interaction between the alkali metal atoms and organic fragments occurs as a homogeneous reaction in the gas phase, or if it is purely a surface phenomenon. Currently, there is no conclusive evidence to determine which mechanism actually takes place.

For specific nitrogen-phosphorus detection, a hydrogen flow rate of $\leq$6 cm^3/min is normally required. The response and background current of the NPD also depend on the air flow rate. Generally, the response decreases with increasing air flow rate.

c. Mass Spectrometer

A mass spectrometer is the most powerful tool available for the chemical analysis of samples because of its high selectivity and sensitivity. The mass spectrometer can be used as a selective detector in the selected-ion monitoring mode for quantitative analysis with a detection limit on the order of picograms. It is also useful for qualitative analysis, because it gives information for identification of organic compounds and elucidation of their structure.

Combined GC-MS is a well established, routinely used technique. A combined SFC-MS will accrue the same benefit as found in GC-MS. However, requirements for SFC-MS interface are more difficult to fulfill than those for the GC-MS interface because (1) the mobile-phase flow rates generated from supercritical fluid are higher than those of GC and (2) the requirements to maintain supercritical fluid conditions in the SFC-MS interface are more stringent than to maintain gas for GC-MS. There are several main requirements:

- The interface between the SFC and the MS must be capable of handling the flow rates generated from the mobile phase.
- The solute must be transported from the column into the MS ion source without altering its chemical nature.
- The resolution obtained with the SFC-MS system should be the same as is obtained with conventional SFC detection.

A general diagram (Fig. 4) of a capillary SFC-MS interface shows a 50 μm ID fused fritted silica restrictor connected to the end of the capillary column via a zero-dead-volume union. The restrictor is inserted

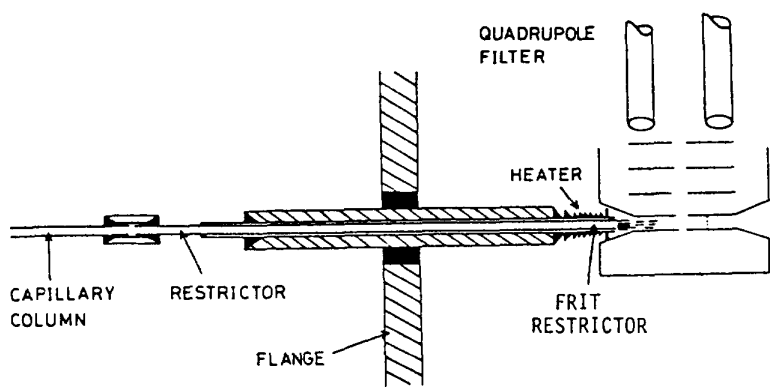


Fig. 4. Diagram of Capillary SFC-MS Interface. (Adapted from [GAMES].)

into the probe and sealed into position so that the restrictor and probe tips are aligned. The probe is inserted into the manifold via a vacuum lock until the tip is seated 10 mm outside the ion source chamber. The restrictor and probe tips are directly heated to prevent solute precipitation during eluant decompression.

d. Ultraviolet-Visible Detector

The ultraviolet-visible detector (UV-Vis) is a nondestructive and concentration-dependent detector. It is the most widely used detector in liquid chromatography. Because most organic compounds have some useful absorption in the UV region (190-600 nm) of the spectrum, this detector is fairly wide in application. However, the sensitivity depends on how strongly the sample absorbs the light signal, and what the availability of a transparent mobile phase is at the wavelength of maximum absorption.

Sample concentration in the flow cell is related to the fraction of transmitted light through the cell by Beer's Law:

$$\log \frac{I}{I_o} = \epsilon bc \tag{19}$$

where I_o = incident light intensity
I = intensity of the transmitted light
ϵ = molar absorptivity
b = cell pathlength
c = sample concentration

Properly designed UV detectors are relatively insensitive to flow and temperature changes except at high sensitivity. The detection limit is a few nanograms of a solute having only moderate UV absorbance. The UV detector has a good linear concentration range ($\sim 10^5$).

V. EXPERIMENTAL

A. Equipment

A Lee Scientific Model 622 supercritical fluid chromatograph/gas chomatograph with FID detector was used for most of the work in this study. A schematic diagram of an SFC system is shown in Fig. 5. Split injection was

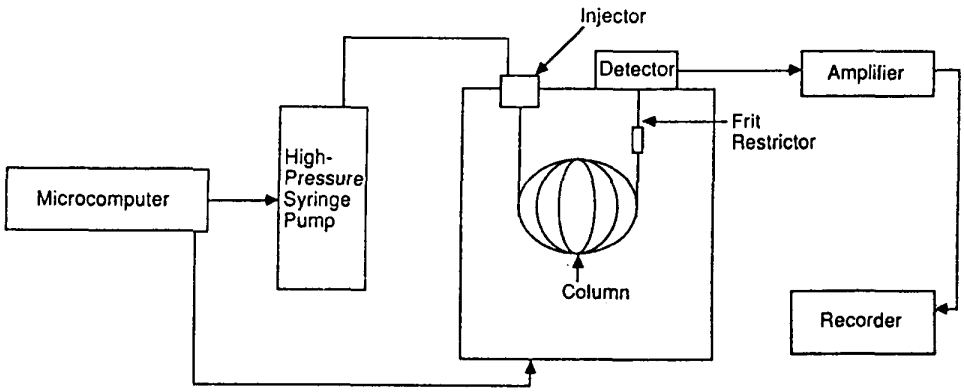


Fig. 5. Schematic Diagram of SFC Instrumentation

done using a 50 μm ID fused silica capillary as a split restrictor (20:1 split ratio). A 50 μm ID frit restrictor was used to control the column flow rate. Experimental conditions were:

1) Carrier fluid of SFC grade CO_2 (Scott Speciality Gas). Linear flow rate was controlled by the length of the frit restrictor (usually 10 times above the minimum linear velocity).

2) Injection temperature at room temperature.

3) Density (pressure) program: set initial valve at 0.25 g/mL; hold for 5 to 10 min (dependent on the length of frit restrictor); increase at 0.01 g/mL/min to 0.55 g/mL; hold for 2 min.

4) Oven temperature of 110°C.

5) Detector temperature of 325°C.

Lee Scientific superbond capillary columns were used. Table 2 lists the characteristics of the columns that were tested in this study.

B. Reagents

The bulk of the CMPO used in this study was purchased from M&T Chemical Company; its purity was defined as solvent-extraction (SX) grade in ANL R&D performed for Westinghouse Hanford [LEONARD], but it is described as crude CMPO in this report. A second sample of CMPO was prepared by Occidental Chemical Company (Glad Island, NY) and was supplied to us by E. P. Horwitz, Chemistry Division, ANL. Gold label TBP (99+% purity) and reagent grade TBP

Table 2. Characteristics of Tested Columns

Stationary Phase	Film Thickness, μm	Length, m	Internal Diameter (ID), μm
SB-Octyl-50	0.25	10	50
SB-Methyl-100	0.25	10	50
SB-Methyl-100	0.25	20	100
SB-Phenyl-5	0.25	20	100
SB-Phenyl-50	0.25	10	50
SB-Biphenyl-30	0.25	20	50

(99%) were obtained from Aldrich Chemical Company. Dichloromethane (HPLC or GC grade from Aldrich) is a common solvent for GC and SFC because it is only slightly retained in the column, and most organic compounds can be easily dissolved in dichloromethane.

C. Purification of CMPO

Purification of CMPO was performed by the method reported by Horwitz et al. [HORWITZ] but with slight modification. One hundred-twenty grams of ~92% pure CMPO was dissolved into 250 mL of n-heptane. Twenty-six grams of Dowex AG-MP50, which had been dehydrated and equilibrated with heptane, was added to the heptane solution. The mixture was stirred for one hour at room temperature. After an hour, 50 g of dehydrated Amberlyst A-26 resin in the hydroxide form, which had also been equilibrated with heptane, was added to the mixture. Stirring was continued for one and one-half hour at room temperature. The resin was removed by filtration. The heptane solution was washed with 0.25M Na_2CO_3 (2:1 O/A*), 0.1M HNO_3 (O/A = 2), and H_2O (O/A = 1) and dried overnight with anhydrous Na_2SO_4. After filtration, a fraction of the heptane was removed by rotatory evaporation. The solution was stored in a freezer. Crystals found at the bottom of the beaker after three days were removed from the mother liquor by filtration and dried under vacuum. The final weight of the purified CMPO was 81 g.

Multiple recrystallizations were performed by repeating the above procedure.

D. Decomposition of CMPO

The white crystalline CMPO (crude or purified) was sealed under vacuum in a glass tube and heated in an oven with the temperature maintained at 190°C for 15 h. During treatment, the CMPO changed to brown liquid. It solidified on standing at room temperature to a pale brown solid.

*O/A = organic-to-aqueous phase ratio.

VI. RESULTS

As discussed above, several parameters must be optimized to produce a successful SFC analysis. The optimization of these parameters is discussed below.

A. Temperature

Carbon dioxide was used as the mobile phase in these studies because of its inertness toward both neutral and acidic compounds and its favorable critical parameters (P_c = 73.8 atm and T_c = 31.3°C), which makes analysis at low temperature possible. The CMPO is a thermally unstable compound that will decompose at ~180°C. Therefore, a study of column temperature effects is very important to ensuring that no decomposition of CMPO is observed inside the column. The five chromatograms in Figs. 6-10 were all run under the same condition of varying the pressure between 100 atm and 250 atm at a rate of 2 atm/min, but the temperatures were varied. These chromatograms show that no decomposition of CMPO was observed between 80°C and 120°C.

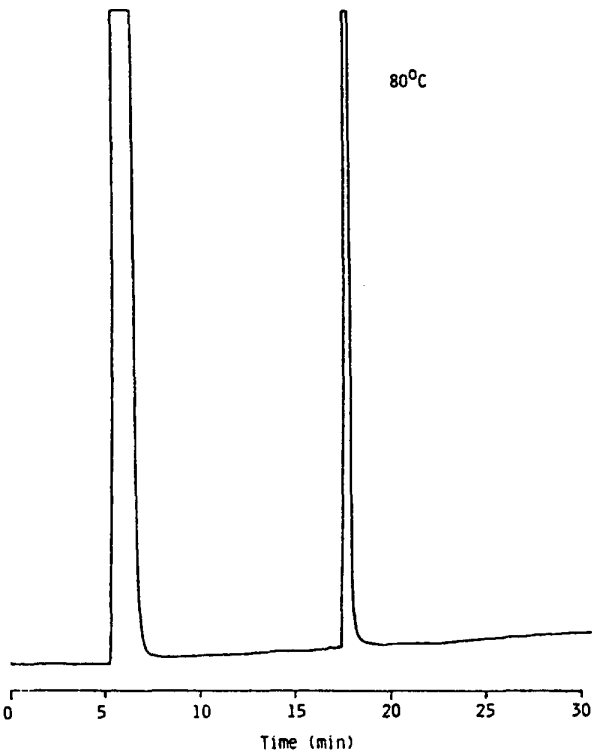


Fig. 6.

Supercritical Fluid Chromatogram of CMPO at 80°C. Experimental conditions: 50 μm ID x 10 m length SB-methyl-100 column. Pressure program from 100 to 250 atm, ramped at 2 atm/min.

Other observations are made for these chromatograms. At a given pressure, the retention time of the solvent (CH_2Cl_2) decreases as the oven temperature increases. This indicates that diffusion is the primary effect controlling the retention time of CH_2Cl_2. On the other hand, the lower the oven temperature, the faster the CMPO elutes from the column. This is explained by the density of the mobile phase, CO_2, being inversely proportional to temperature at a fixed pressure. With the same pressure, the

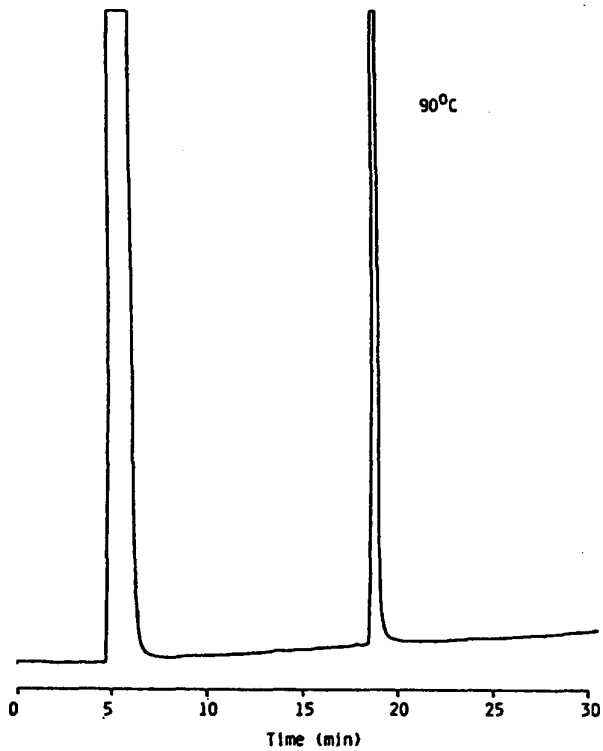
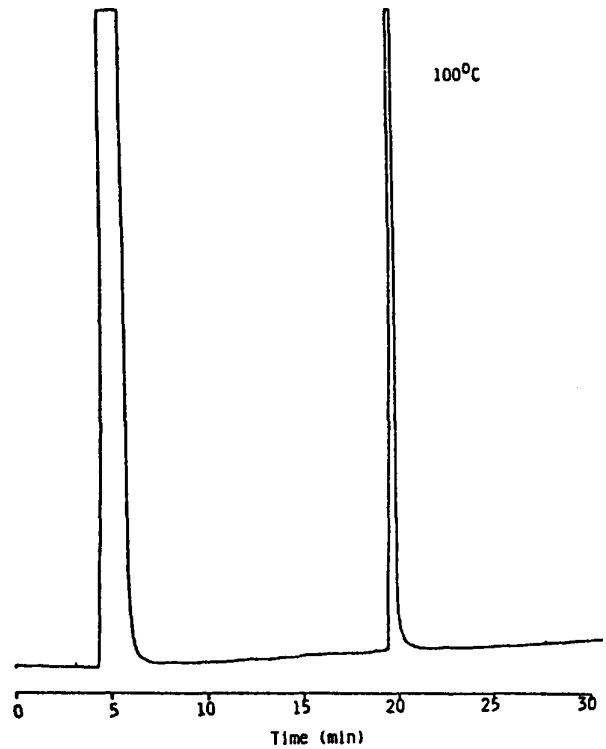


Fig. 7.

Supercritical Fluid Chromatogram of CMPO at 90°C. Experimental conditions: 50 μm ID x 10 m length SB-methyl-100 column. Pressure program from 100 to 250 atm, ramped at 2 atm/min.

Fig. 8.

Supercritical Fluid Chromatogram of CMPO at 100°C. Experimental conditions: 50 μm ID x 10 m length SB-methyl-100 column. Pressure program from 100 to 250 atm, ramped at 2 atm/min.



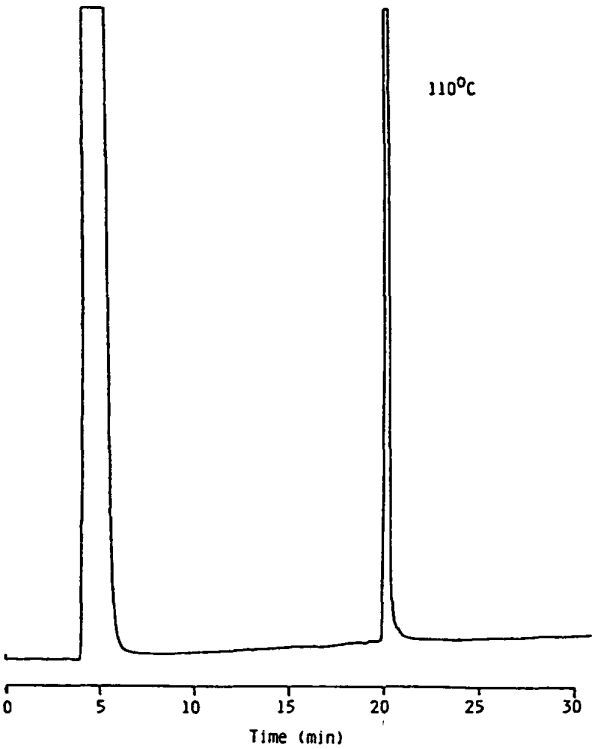
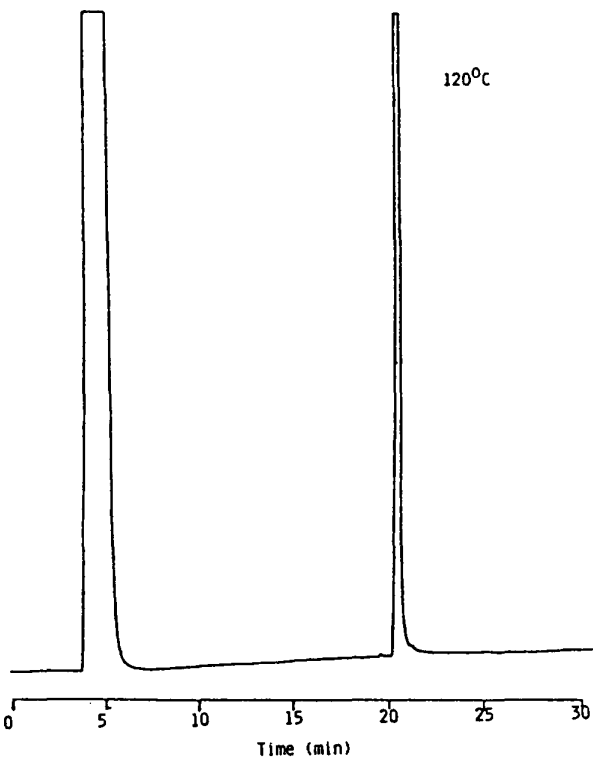


Fig. 9.

Supercritical Fluid Chromatogram of CMPO at 110°C. Experimental conditions: 50 μm ID x 10 m length SB-methyl-100 column. Pressure program from 100 to 250 atm, ramped at 2 atm/min.

Fig. 10.

Supercritical Fluid Chromatogram of CMPO at 120°C. Experimental conditions: 50 μm ID x 10 m length SB-methyl-100 column. Pressure program from 100 to 250 atm, ramped at 2 atm/min.



density of carbon dioxide is higher at lower temperatures (e.g., at 100 atm, the density of CO_2 is 0.2282 g/mL at 80°C and 0.1698 g/mL at 120°C). The supercritical fluid character of CO_2 changes from that of a nonpolar solvent (e.g., hexane) to that of a polar solvent (e.g., methylene chloride) when the density of CO_2 increases. Therefore, at a given pressure, more rapid chromatographic elution of CMPO is expected at lower temperature because the solubility of CMPO in CO_2 increases, increasing the partitioning of CMPO to the mobile phase [ASHRAF-KHORASSANI].

Elution occurs at lower densities when the separation is performed at elevated temperatures, and high efficiencies are obtained. In addition, diffusion of solutes in the mobile and stationary phases normally increases with temperature, also resulting in improved efficiencies [FIELD, CHESTER]. Generally, it is recommended that SFC analyses be performed at the maximum temperature that the solutes can withstand without risk of degradation.

B. Column Selection

Different stationary phases have been evaluated to determine the best resolution of the TRUEX solvent mixtures. Stationary phases that were tested are 50% octyl-50% methyl, 100% methyl, 5% phenyl-95% methyl, 50% phenyl-50% methyl, and 30% biphenyl-70% methyl polysiloxane. Of the columns tested, the 50% octyl-50% methyl is the least polar, and the 30% biphenyl-70% methyl is the most polar. The resolution of CMPO impurities is poor for the 50% octyl-50% methyl column, while, for the 50% phenyl-50% methyl and 30% biphenyl-70% methyl columns run under the same conditions, CMPO was completely retained by the column ($t_r \sim \infty$). Since the 100% methyl column shows a slightly better resolution of the impurities present in CMPO than the 5% phenyl-95% methyl column, the 100% methyl column was chosen for further analysis.

C. Peak-Size Standardization

There are four common techniques of peak-size standardization: area normalization, internal standard, external standard, and standard addition. An explanation of each method can be found elsewhere [MILLER]. The composition of an unknown mixture may be estimated from the peak-area percentage of each component in the chromatogram. However, because the detector does not respond equally to each component, for quantitative analysis, a response factor is necessary to normalize the peak area to each component's mass.

The internal standard technique selected for this study is particularly useful in quantitative analysis. It minimizes quantitative error due to sample preparation and injection, allows the quantitation of one or more components in the sample matrix, and requires that chromatographic resolution only be optimized for the separation of the component of interest and the internal standard.

Different alkane chain lengths (C-16, C-18, C-20, C-24 and C-30) have been considered as the internal standard. Results show that C-24 is the most appropriate standard, since its retention time does not overlap with any impurity from TBP and CMPO when they are analyzed individually or together (Fig. 11). Appendix E describes the method we used for the C-24 internal standard.

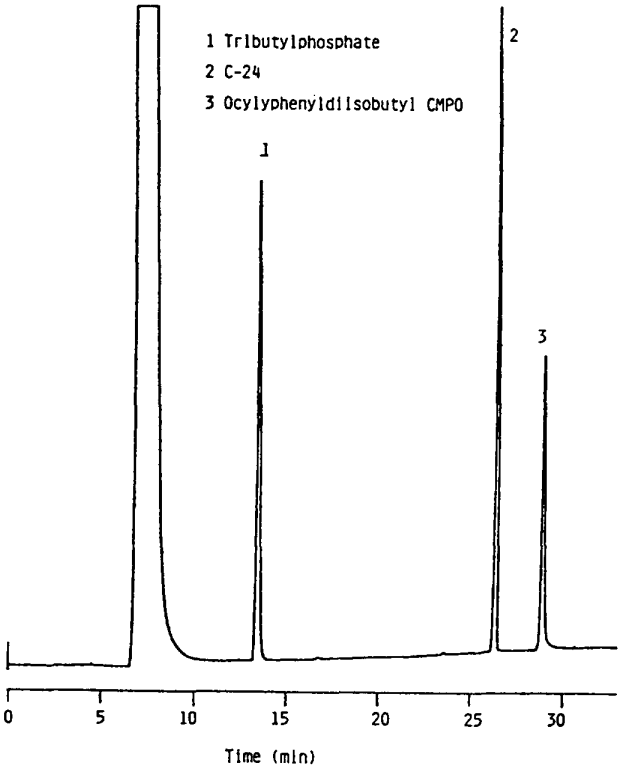


Fig. 11.

Supercritical Fluid Chromatogram of Mixture of TBP, C-24, and CMPO. Experimental conditions: 100 μm ID x 20 m length SB-methyl-100 column. Density program from 0.25 g/mL to 0.55 g/mL, ramped at 0.01 g/mL/min. Oven temperature at 110°C.

D. Analysis of CMPO Purity

Since impurities in CMPO can drastically affect metal distribution ratio measurements, it is very important to know the purity of the CMPO. To test its purity, the crude (or SX-grade) CMPO was dissolved in CH_2Cl_2 (without derivatization) and C-24 was added as an internal standard. A typical chromatogram of the crude CMPO is displayed in Fig. 12. Besides CMPO and C-24 peaks, twelve other peaks are found in this crude material. The purity of this lot of CMPO was determined to be 96%.

When the white crystals of crude CMPO were placed in a sealed vacuum glass tube and heated in an oven with the temperature maintained at 190°C for 15 h, ten additional peaks appeared in its chromatogram (Fig. 13). The decomposed sample was found to contain 90% CMPO.

Purification and recrystallization of the crude CMPO were observed to decrease its impurity content greatly (Fig. 14). Its purity was determined to increase from 96% to 99+%.

The purified CMPO was also heated in an oven under conditions identical to the crude CMPO. Less than one percent of the CMPO (Fig. 15) was lost, compared to a 6% loss for the crude CMPO. Since the experiments were performed under the same conditions, it appears that some impurities in the crude CMPO must catalyze the decomposition of CMPO. Optimum conditions for CMPO analysis are described in Appendix A.

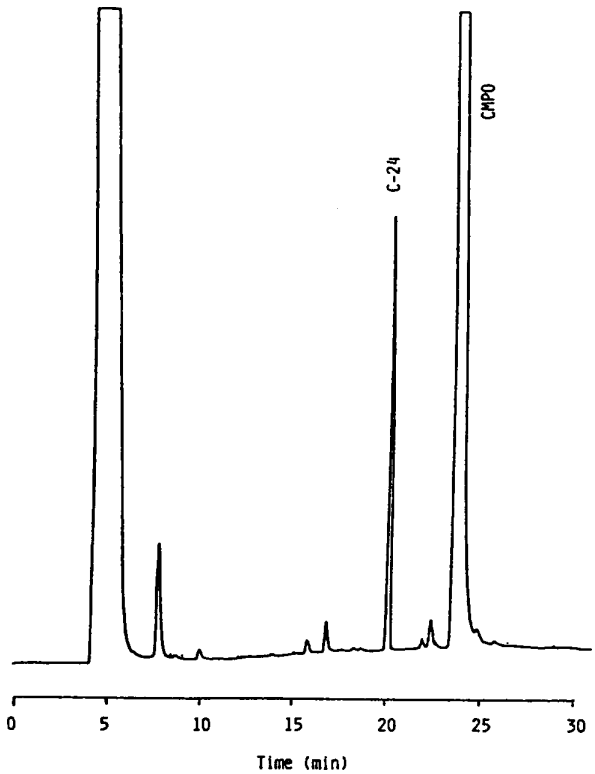


Fig. 12.

Supercritical Fluid Chromatogram of Crude CMPO. Experimental conditions: 100 μm ID x 20 m length SB-methyl-100 column. Density program from 0.25 g/mL to 0.55 g/mL, ramped at 0.01 g/mL/min. Oven temperature at 110°C.

E. Analysis of TBP Purity

Two kinds of TBP, a gold label and a reagent grade, were tested in this study. In the analysis of gold label TBP, several compounds eluted with retention times longer than that of TBP (Fig. 16). Five milliliters of the gold label TBP was contacted three times with equal volumes of 0.25M Na_2CO_3, 0.01M HNO_3, and H_2O, respectively. Figure 17 shows that there were no changes in either peak areas or number of peaks in the chromatogram due to this treatment. This indicates that these high-elution-time compounds are likely trialkylphosphates with molecular weights greater than TBP. Acidic and other water-soluble, low-molecular-weight phosphorus compounds would have been removed by these treatments.

A chromatogram of the reagent-grade TBP (Fig. 18) shows more peaks at longer elution times than gold label TBP, indicating the presence of a greater abundance of these impurities.

F. Quantitative Analysis of CMPO-TBP Mixtures

To minimize matrix effects, mixtures of TBP and CMPO were used to generate a standard curve calibration. Table 3 shows the concentrations of the solution used and the amounts injected.

The ratios of the areas of TBP/C-24 and CMPO/C-24 were first calculated from the five replicate injections for each of the solutions used for the calibration curves. The mean values obtained from the area ratios were

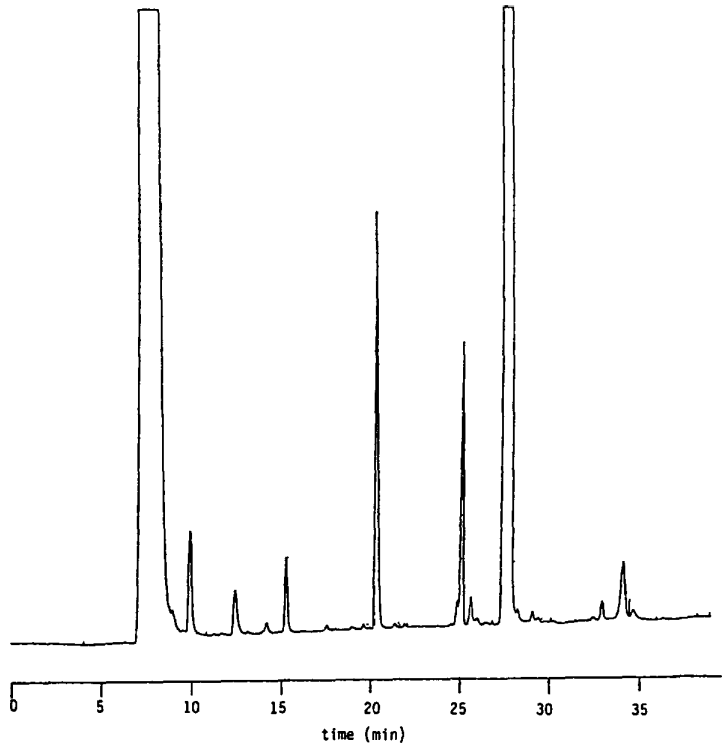


Fig. 13. Supercritical Fluid Chromatogram of Thermally Decomposed Crude CMPO. Experimental conditions: 100 μm ID x 20 m length SB-methyl-100 column. Density program from 0.25 to 0.55 g/mL, ramped at 0.01 g/mL/min. Oven temperature at 110°C.

plotted against the amount injected. The calibration curves (actually straight lines) shown in Fig. 19 have slopes of 8.3 and 9.0 for TBP and CMPO, respectively. As can be seen in Fig. 19, the TBP and CMPO detector response is linear over the range of concentrations in this study. The relative standard deviations of the area ratios are reported in Table 4.

The concentration of CMPO was measured over a range of 0.01 to 0.5M with an uncertainty of ±2% in the absence or presence of TBP. The mole ratio of TBP/CMPO was varied from 1 to 8 with no loss in precision or accuracy. Appendix B gives optimum SFC conditions for quantitating CMPO and TBP in CMPO/TBP mixtures.

G. Analysis of TRUEX Solvents

Two TRUEX solvents, TRUEX-TCE (0.75M TBP, 0.25M CMPO in TCE) and TRUEX-NPH (1.4M TBP, 0.20M CMPO in NPH), are typically used in TRUEX processing. Their analyses are performed in similar manners, but TRUEX-TCE analyses appear to be more straightforward and are done with higher precision. The results of each study are discussed below.

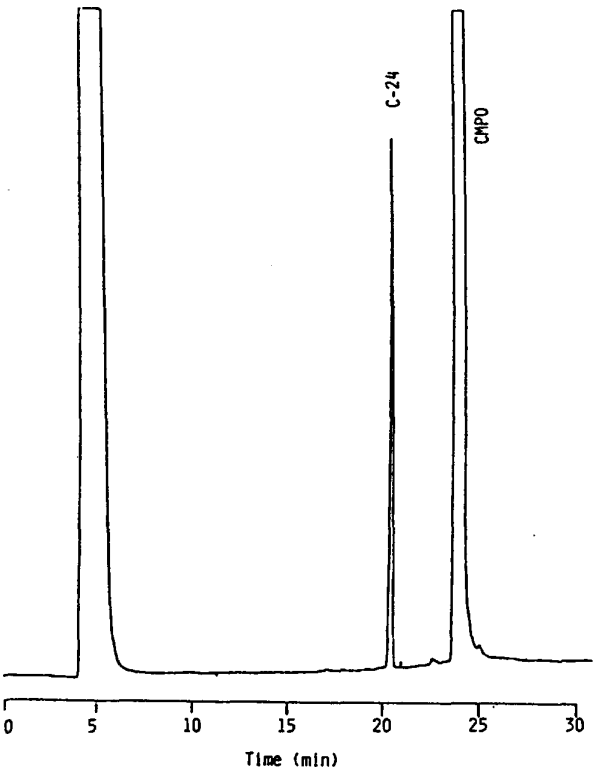


Fig. 14.

Supercritical Fluid Chromatogram of Purified and Recrystallized CMPO. Experimental conditions: 50 μm ID x 10 m length SB-methyl-100 column. Density program from 0.25 to 0.55 g/mL, ramped at 0.01 g/mL/min. Oven temperature at 110°C.

1. TRUEX-TCE Analysis

Figure 20 shows a typical chromatogram of TRUEX-TCE solvent dissolved in dichloromethane. Both CH_2Cl_2 and TCE are eluted at the same retention time; under these experimental conditions, TCE cannot be separated from CH_2Cl_2. The TBP and CMPO are well separated from each other and also from the diluent. Table 5 shows SFC data from ten replicate injections of TRUEX-TCE solutions. The standard deviation of the elution time of the three solutes (TBP, C-24, and CMPO) is less than two-tenths of a minute. The relative standard deviation of the peak area of these solutes is below 3%. The precision obtained by using C-24 as an internal calibration of TRUEX-TCE is shown in Table 6. The concentration of CMPO and TBP can be analyzed according to the procedure described in Appendix C.

2. TRUEX-NPH Analysis

For TRUEX-NPH (Fig. 21), all components of the mixed hydrocarbon diluent are well separated from CH_2Cl_2. The five major components of the NPH diluent are normal hydrocarbons with carbon chain lengths of 11 to 15. The TBP is eluted after the NPH components, with the separation factor between TBP and C-15 being <2. The C-24 standard and CMPO are eluted with significantly longer retention times. Table 7 shows SFC data for ten duplicate injections of TRUEX-NPH solutions. The reproducibility of elution time of C-12, C-13, C-14, C-15, TBP, C-24, and CMPO is less than two-tenth of a minute. The relative standard deviation of the peak area of these seven solutes is below 5.5%. The precision obtained by using C-24 as an internal standard to

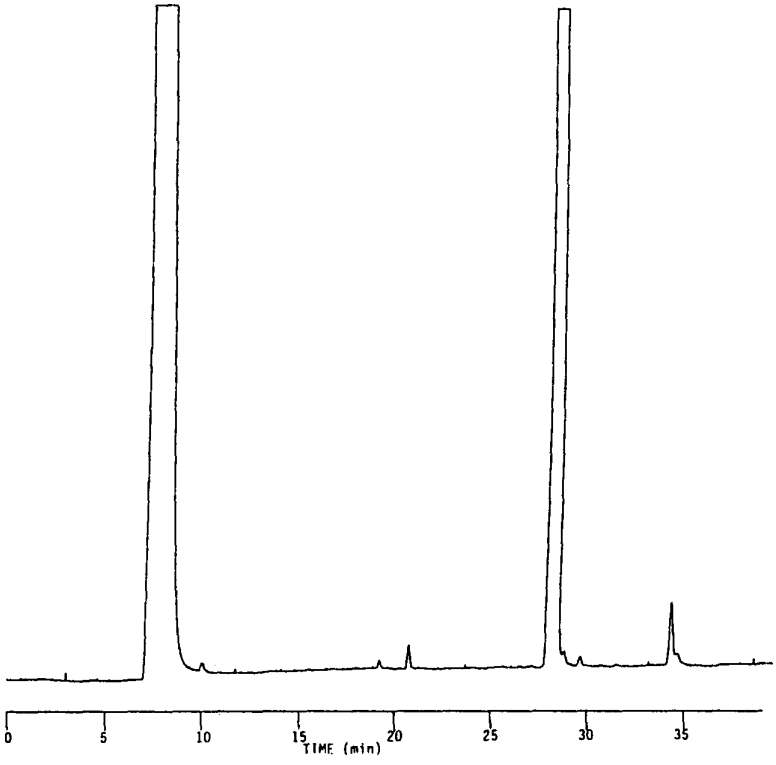


Fig. 15. Supercritical Fluid Chromatogram of Thermally Decomposed Purified CMPO. Experimental conditions: 100 μm ID x 20 m length SB-methyl-100 column. Density program from 0.25 to 0.55 g/mL, ramped at 0.01 g/mL/min. Oven temperature at 110°C.

calibrate TRUEX-NPH is shown in Table 8. The concentrations of CMPO and TBP can be analyzed according to the procedure described in Appendix D.

H. Analysis and Identification of Impurities

No development of an analytical technique is complete without at least some attention being paid to the behavior of possible impurities in the compound of interest. The following limited studies were performed to give an indication of the SFC behavior of a series of organophosphorus compounds that act as stand-ins for those likely present in impure CMPO and TBP.

Figure 22 is a chromatogram of a mixture of seven organic phosphorus compounds: dibutylphosphite, tributylphosphate, diphenylphosphine, diphenylphosphite, methyldiphenylphosphine, diphenylphosphine oxide, and CMPO. Under conditions chosen for this analysis, diphenylphosphine (peak #4) and methyldiphenylphosphine (peak #5), which differ by the substitution of a hydrogen by a methyl group, have baseline resolution. Unfortunately, under these experimental conditions, diphenylphosphite and methyldiphenylphosphine cannot be separated from each other. This situation could possibly be improved by using another stationary phase.

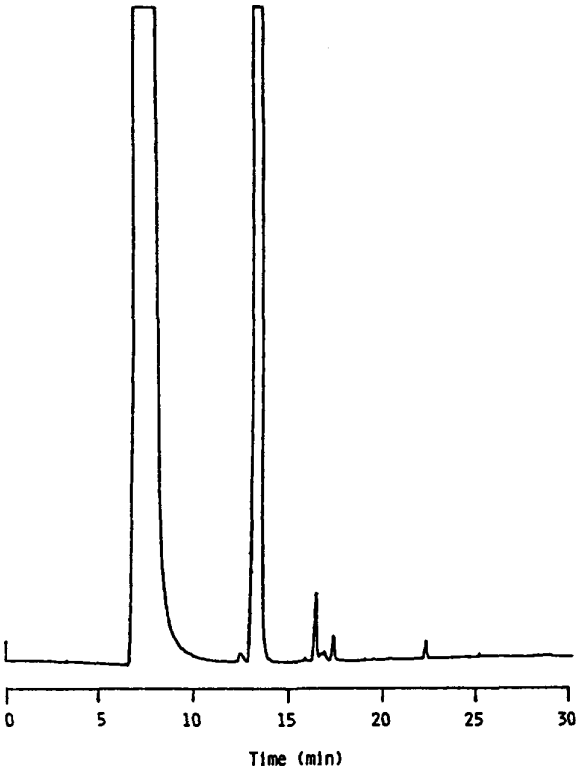
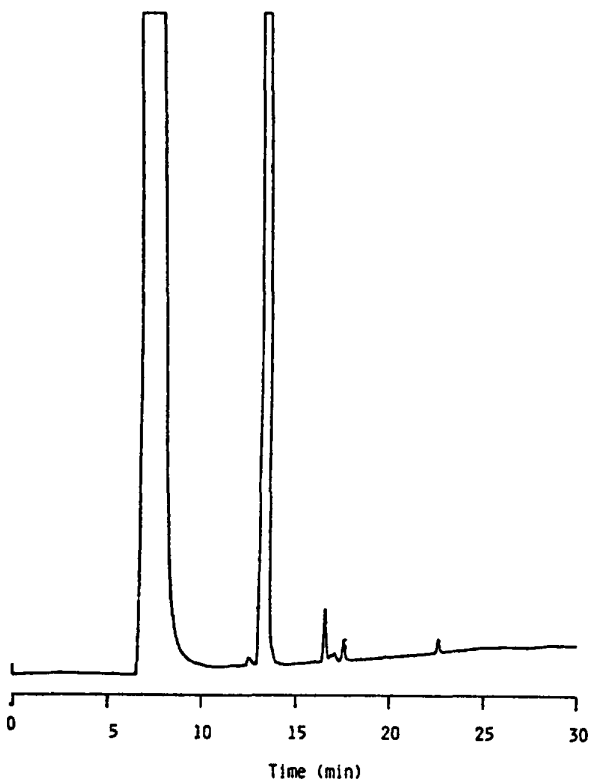


Fig. 16.

Supercritical Fluid Chromatogram of Gold Label TBP. Experimental conditions: 100 μm ID x 20 m length SB-methyl-100 column. Density program from 0.25 to 0.55 g/mL, ramped at 0.01 g/mL/min. Oven temperature at 110°C.

Fig. 17.

Supercritical Fluid Chromatogram of Carbonate-Washed Gold Label TBP. Experimental conditions: 100 μm ID x 20 m length SB-methyl-100 column. Density program from 0.25 to 0.55 g/mL, ramped at 0.01 g/mL/min. Oven temperature at 110°C.



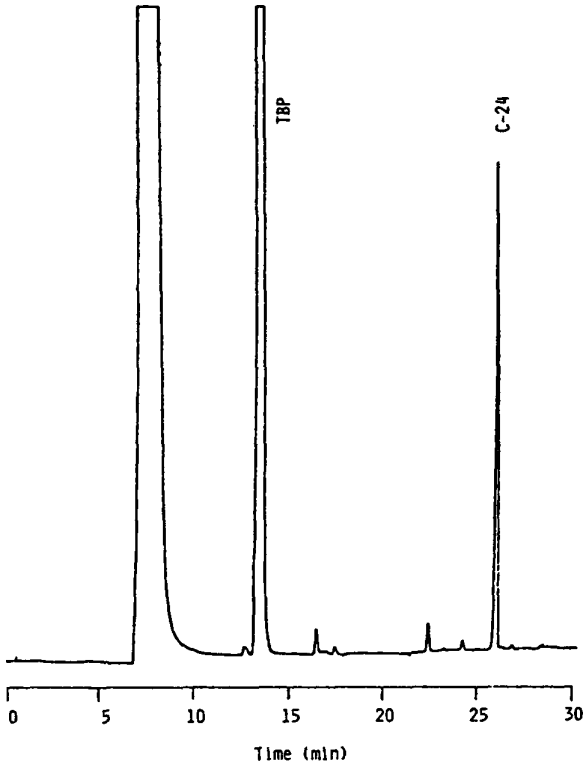


Fig. 18.

Supercritical Fluid Chromatogram of Reagent-Grade TBP. Experimental conditions: 100 μm ID x 20 m length SB-methyl-100 column. Density program from 0.25 to 0.55 g/mL, ramped at 0.01 g/mL/min. Oven temperature at 110°C.

Table 3. Solutions of TBP, CMPO, and C-24 Used in Generating the Calibration Curves

	TBP		CMPO		C-24	
Solution[a]	μg/mL	Injected (μg)	μg/mL	Injected (μg)	μg/mL	Injected (μg)
1	180.00	0.09	100.00	0.050	210	0.11
2	240.00	0.12	130.00	0.065	210	0.11
3	280.00	0.18	200.00	0.100	210	0.11
4	1200.00	0.60	650.00	0.325	210	0.11
5	3600.00	1.80	2000.00	1.000	210	0.11
6	6000.00	3.00	3200.00	1.600	210	0.11

[a]Five replicate injections were performed with each solution.

Since phosphines and phosphine oxides have different polarities, leading to different interaction with the stationary phase, they will have different retention times. The diphenylphosphine oxide has a longer retention time than diphenylphosphine. Literature results show that SFC can be used to analyze labile carboxylic acid [MARKIDES]; however, the injection of strong acids (such as nitric and alkyl phosphoric, phosphonic, and phosphinic acids) into the column is not recommended. Because these acids will attack the backbone of the column and will be retained, the lifetime of the column will be shortened. In some instances, the column can be regenerated by repeated injection of the solvent at high pressure. If not, a new column may need to be installed.

Table 4. Precision of Measurements in the Internal-Standard Method of Calibration

	Area Ratios			
	TBP/C-24		CMPO/C-24	
Solution	Avg.	% RSD[a]	Avg.	% RSD[a]
1	0.74	0.13	0.43	0.89
2	0.98	0.89	0.56	2.02
3	1.58	0.24	0.90	0.27
4	4.96	0.30	3.11	0.43
5	15.17	0.18	9.49	1.22
6	24.96	0.32	14.20	0.73

[a] Percent relative standard deviation.

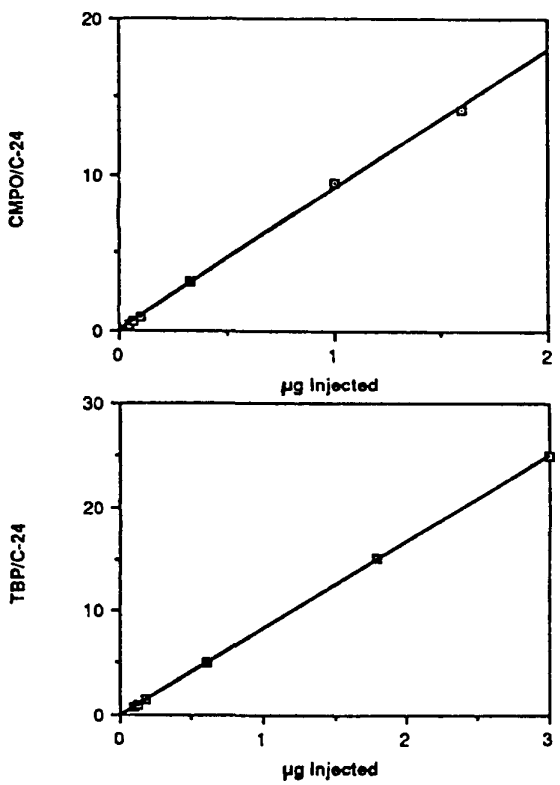


Fig. 19.

Area Ratio of CMPO/C-24 vs. Amount of CMPO Injected and Area Ratio of TBP/C-24 vs. Amount of TBP Injected

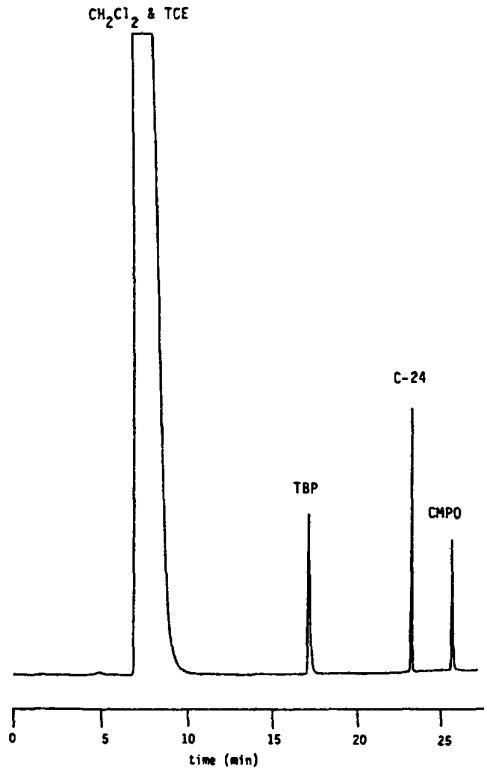


Fig. 20.

Supercritical Fluid Chromatogram of the TRUEX-TCE Solvent. Experimental conditions: 50 μm ID x 10 m SB-methyl-100 column. Density program from 0.25 to 0.55 g/mL, ramped at 0.01 g/mL/min. Oven temperature at 110°C.

Table 5. Data from Supercritical Fluid Chromatography of TRUEX-TCE

	TBP		C-24		CMPO	
	Time, Min	Peak Area	Time, Min	Peak Area	Time, Min	Peak Area
Run 1	16.85	265947	23.22	250357	25.74	151260
Run 2	17.00	271348	23.31	256609	25.82	163178
Run 3	17.08	262365	23.36	246051	25.86	149365
Run 4	17.12	259790	23.38	242271	25.88	150421
Run 5	17.15	259787	23.40	242293	25.90	149151
Run 6	17.27	257223	23.47	244149	25.99	149415
Run 7	17.33	269579	23.53	250906	26.02	153555
Run 8	17.36	261856	23.55	246041	26.03	153366
Run 9	17.38	262144	23.57	244874	26.05	153249
Run 10	17.41	262753	23.59	246107	26.07	153049
Average	17.20	263279	23.44	246966	25.94	152601
S.D.	0.19	4440	0.12	4455	0.11	4124
% RSD	1.10	1.69	0.51	1.80	0.42	2.70

S.D. = Standard Deviation
% RDS = Percent Relative Standard Deviation (100 x S.D./average)

Table 6. Replicate SFC Measurements of TRUEX-TCE with the Internal Standard Method

	Peak Area (TBP/C-24)	Peak Area (CMPO/C-24)
Run 1	1.062	0.604
Run 2	1.057	0.636
Run 3	1.066	0.607
Run 4	1.072	0.621
Run 5	1.072	0.616
Run 6	1.054	0.612
Run 7	1.074	0.612
Run 8	1.064	0.623
Run 9	1.071	0.626
Run 10	1.068	0.622
Average	1.066	0.618
S.D.	0.007	0.010
% RSD	0.657	1.618

S.D. = Standard Deviation
% RDS = Percent Relative Standard Deviation (100 x S.D./average)

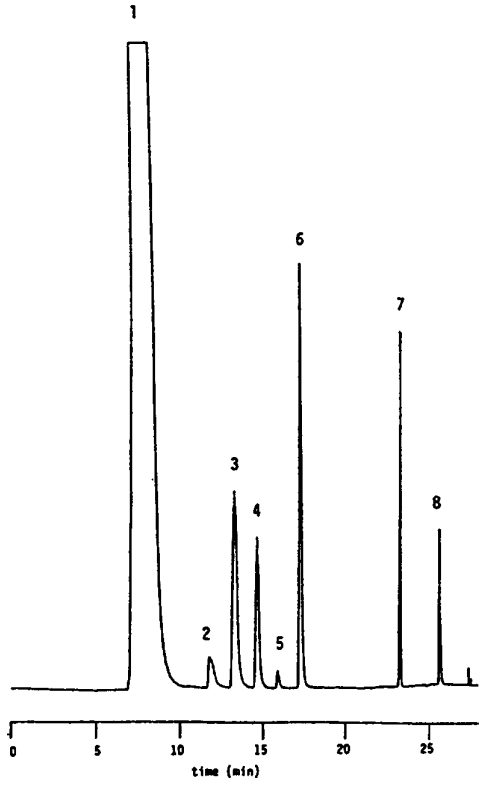


Fig. 21.

Supercritical Fluid Chromatogram of the TRUEX-NPH Solvent:

1) CH_2Cl_2 2) n-$C_{12}H_{26}$
3) n-$C_{13}H_{28}$ 4) n-$C_{14}H_{30}$
5) n-$C_{15}H_{32}$ 6) TBP
7) C-24 Standard 8) CMPO

Experimental conditions: 50 μm ID x 10 m SB-methyl-100 column. Density program from 0.25 to 0.60 g/mL, ramped at 0.02 g/mL/min. Oven temperature at 100°C.

Table 7. Data from Supercritical Fluid Chromatography of TRUEX-NPH

	C-12		C-13		C-14		C-15		TBP		C-24		CMPO	
	Time, min	Peak Area	Time, min	Peak Area	Time, min	Peak Area	Time, min	Peak Area	Time, min	Peak Area	Time, min	Peak Area	Time, min	Peak Area
Run 1	11.27	146807	12.66	733633	14.05	419584	15.38	39144	16.71	788650	23.13	366396	25.66	194711
Run 2	11.36	134624	12.75	676013	14.15	384982	15.46	34257	16.80	719521	23.20	332051	25.73	176591
Run 3	11.47	155722	12.83	727430	14.22	418206	15.55	40404	16.89	756740	23.27	351052	25.79	186284
Run 4	11.54	141071	12.95	701373	14.34	400851	15.65	35674	16.98	747889	23.32	344851	25.83	183747
Run 5	11.55	140522	12.98	685599	14.37	393910	15.68	37322	17.03	735663	23.34	340389	25.85	180676
Run 6	11.58	134454	12.99	677053	14.38	390612	15.70	37337	17.05	725329	23.36	333726	25.87	178088
Run 7	11.59	134842	13.01	680754	14.41	384767	15.72	35823	17.06	726463	23.37	334941	25.87	186396
Run 8	11.59	132013	13.00	672158	14.41	379880	15.71	34529	17.06	710515	23.37	328406	25.87	173535
Run 9	11.24	144543	12.63	726117	14.01	420245	15.32	38104	16.64	769249	23.08	361852	25.59	180851
Run 10	11.26	146935	12.66	716531	14.05	409743	15.37	38518	16.69	760971	23.14	356904	25.65	183444
Average	11.45	141153	12.85	699666	14.24	400278	15.55	37111	16.89	744099	23.26	345057	25.77	182432
S.D.	0.15	7457	0.16	24255	0.16	15661	0.16	2016	0.17	24816	0.11	13386	0.11	5980
% RSD	1.31	5.28	1.25	3.47	1.12	3.91	1.03	5.43	1.01	3.34	0.47	3.88	0.43	3.28

S.D. = Standard Deviation

% RSD = Percent Relative Standard Deviation (100 x S.D./average)

Table 8. Replicate Measurements of TRUEX-NPH with the Internal Standard Method

	Area (TBP/C-24)	Area (CMPO/C-24)
Run 1	2.152	0.531
Run 2	2.167	0.532
Run 3	2.156	0.531
Run 4	2.169	0.533
Run 5	2.161	0.531
Run 6	2.173	0.534
Run 7	2.169	0.557
Run 8	2.164	0.528
Run 9	2.126	0.500
Run 10	2.132	0.514
Average	2.157	0.529
S.D.	0.016	0.015
% RSD	0.742	2.836

S.D. = Standard Deviation
% RDS = Percent Relative Standard Deviation (100 x S.D./average)

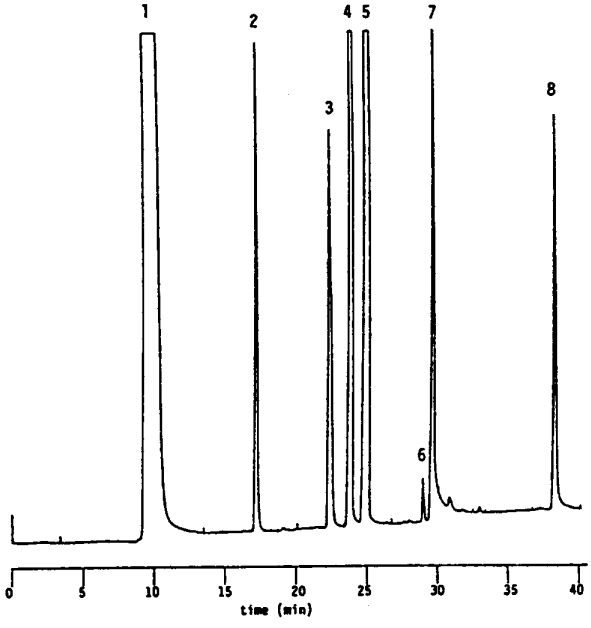


Fig. 22.

Supercritical Fluid Chromatogram of Organophosphorus Compounds:

1) CH_2Cl_2
2) Dibutylphosphite
3) Tributylphosphate
4) Diphenylphosphine
5) Methyldiphenylphosphine
6) Diphenylphosphite
7) Diphenylphosphine Oxide
8) CMPO

Experimental conditions: 50 μm ID x 10 m SB-methyl-100 column. Density program from 0.2 to 0.6 g/mL, ramped at 0.01 g/mL/min. Oven temperature at 110°C.

Future studies will attempt to identify important impurities and degradation products associated with CMPO and the TRUEX-NPH and TRUEX-TCE process solvents. For these studies, the importance of an impurity or degradation product will be based on the effect on the solvent extraction behavior of the TRUEX solvent.

I. Analysis of TBP and CMPO with Other Detectors

As discussed in Sec. IV.B.2, the most universally used detector for both GC and SFC is the FID. Because other detectors are available and may offer advantages in some applications, part of our efforts was directed to identifying the utility of the nitrogen/phosphorus detector, mass spectrometer, and UV detector for analysis of CMPO and TRUEX solvents.

These experiments were performed at Lee Scientific, Salt Lake City, Utah. All the experimental conditions were the same as those used at ANL, except that the linear flow velocities were slightly different due to the different frit restrictors that are used with detectors other than the FID. These differences only slightly affect the resolution of components or retention times.

1. Nitrogen/Phosphorus Detector

Because the NPD is sensitive to CH_2Cl_2, hexane was chosen to dissolve all samples throughout the study of this detector. The detector sensitivity was adjusted so that all hydrocarbons had negative peaks, and all nitrogen-and-phosphorus-containing compounds had positive peaks.

a. TBP

Figure 23 is a chromatogram of gold label TBP dissolved in hexane with a nitrogen/phosphorus detector connected to the SFC. The retention time of TBP was 18 min; another NPD-sensitive compound was measured at a higher retention time (33 min). The signal recorded for TBP is small for the amount of sample injected. The reason TBP does not give a good response on the NPD may be that the phosphorus atom is enclosed by twelve carbon atoms, thereby reducing the contact surface between the phosphorus atom and the alkali-metal-salt bead. This assumption is given validity by the small negative peak in front of the TBP peak, which indicates that hydrocarbon is being measured at the surface of the bead.

b. CMPO

Five different CMPO samples (crude CMPO; decomposed, crude CMPO; purified CMPO; decomposed, purified CMPO; and crude CMPO from Occidental) were analyzed by the SFC-NPD (Figs. 24-28).

Comparison of the chromatograms generated from the FID and from the NPD shows that, as expected, fewer peaks are detected by the NPD. The NPD detected six fewer peaks for crude CMPO than the FID (Fig. 24 vs. 12); ten fewer peaks for decomposed, crude CMPO (Fig. 25 vs. Fig. 13); one fewer peak for purified CMPO (Fig. 26 vs. Fig. 14); and two fewer peaks for decomposed, purified CMPO (Fig. 27 vs. Fig. 15). An exception is the CMPO produced by Occidental; the number of peaks is the same in both detectors for this CMPO sample (Fig. 28 vs. 29).

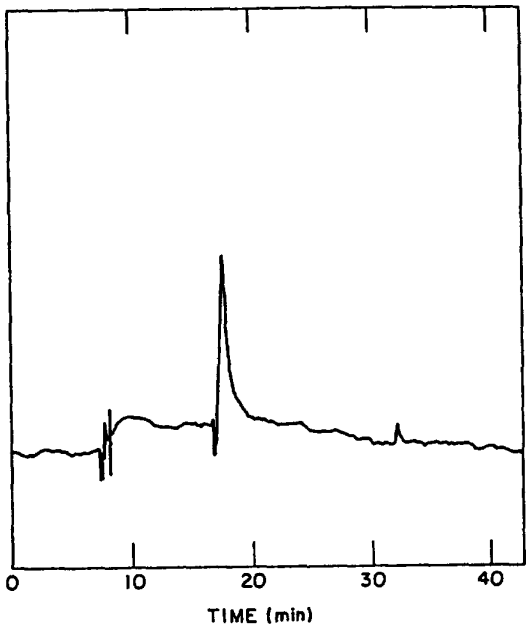
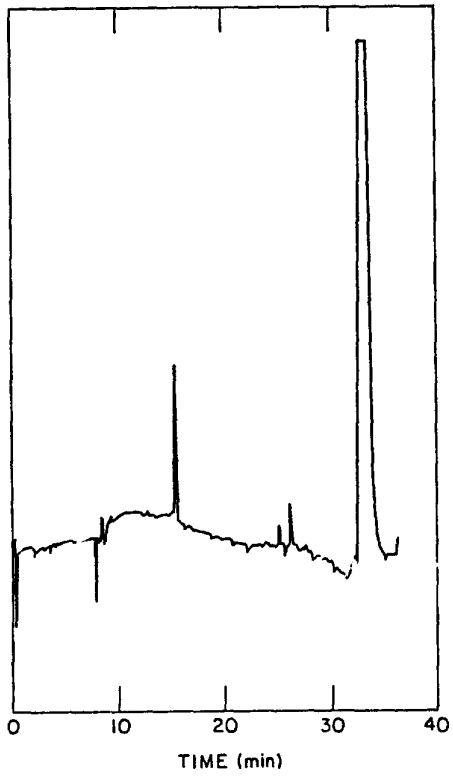


Fig. 23.

Supercritical Fluid Chromatogram of Aldrich Gold Label TBP Obtained with NPD. Experimental conditions: 50 μm ID x 10 m length SB-methyl-100 column. Density program from 0.25 to 0.55 g/mL, ramped at 0.01 g/mL/min. Oven temperature at 100°C.

Fig. 24.

Supercritical Fluid Chromatogram of Crude CMPO Obtained with NPD. Experimental conditions: 50 μm ID x 10 m length SB-methyl-100 column. Density program from 0.25 to 0.55 g/mL, ramped at 0.01 g/mL/min. Oven temperature at 110°C.



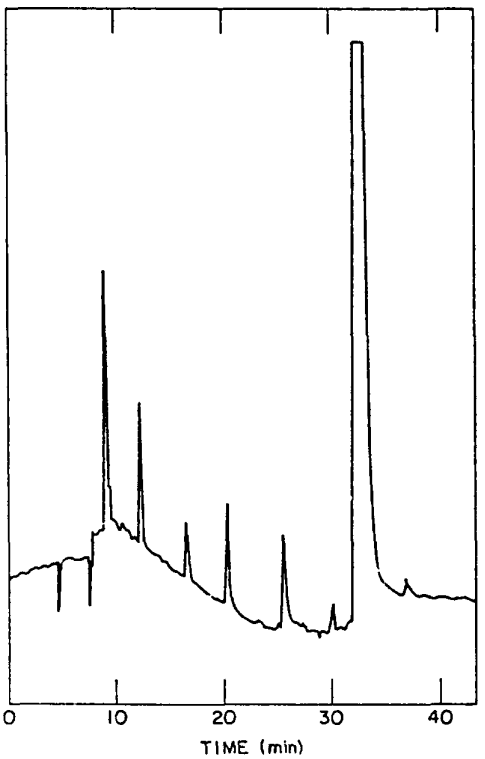


Fig. 25.

Supercritical Fluid Chromatogram of Decomposed, Crude CMPO Obtained by NPD. Experimental conditions: 50 μm ID x 10 m length SB-methyl-100 column. Density program from 0.25 to 0.55 g/mL, ramped at 0.01 g/mL/min. Oven temperature at 110°C.

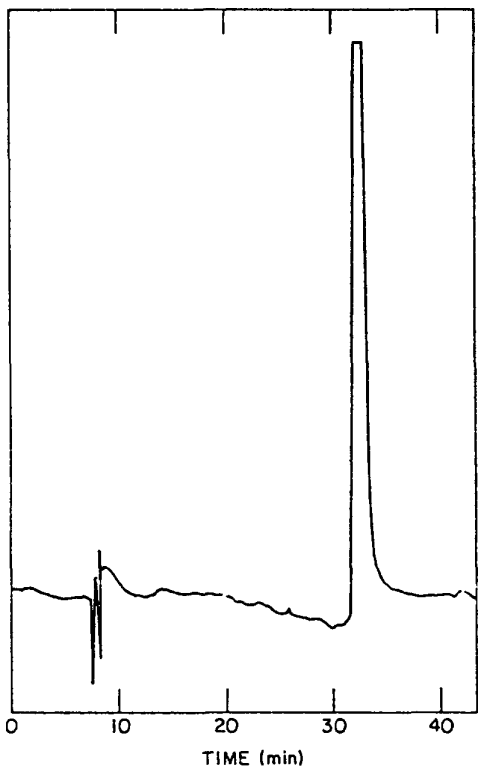


Fig. 26.

Supercritical Fluid Chromatogram of Purified CMPO Obtained with NPD. Experimental conditions: 50 μm ID x 10 m length SB-methyl-100 column. Density program from 0.25 to 0.55 g/mL, ramped at 0.01 g/mL/min. Oven temperature at 110°C.

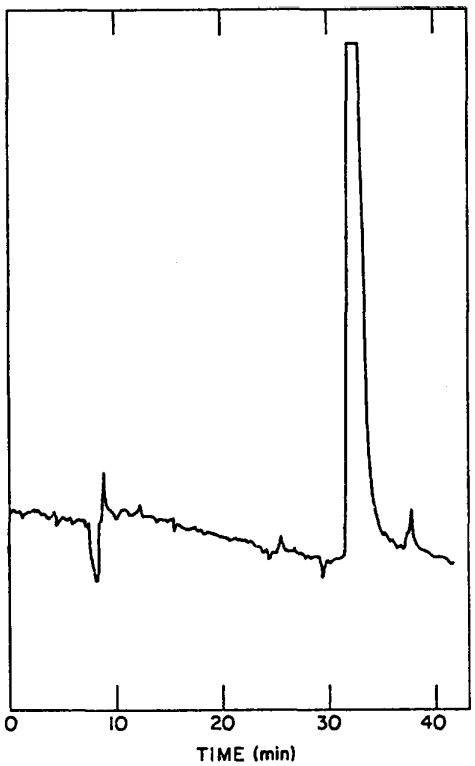
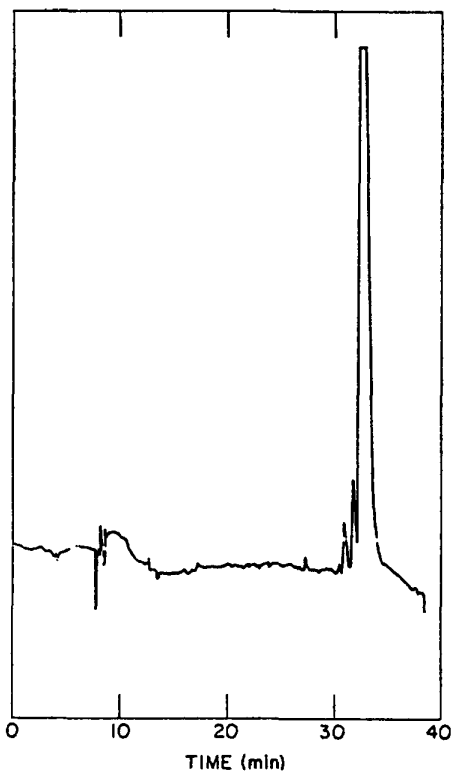


Fig. 27.

Supercritical Fluid Chromatogram of Decomposed, Purified CMPO Obtained with NPD. Experimental conditions: 50 μm ID x 10 m length SB-methyl-100 column. Density program from 0.25 to 0.55 g/mL, ramped at 0.01 g/mL/min. Oven temperature at 110°C.

Fig. 28.

Supercritical Fluid Chromatogram of Occidental Crude CMPO Obtained with NPD. Experimental conditions: 50 μm ID x 10 m length SB-methyl-100 column. Density program from 0.25 to 0.55 g/mL, ramped at 0.01 g/mL/min. Oven temperature at 110°C.



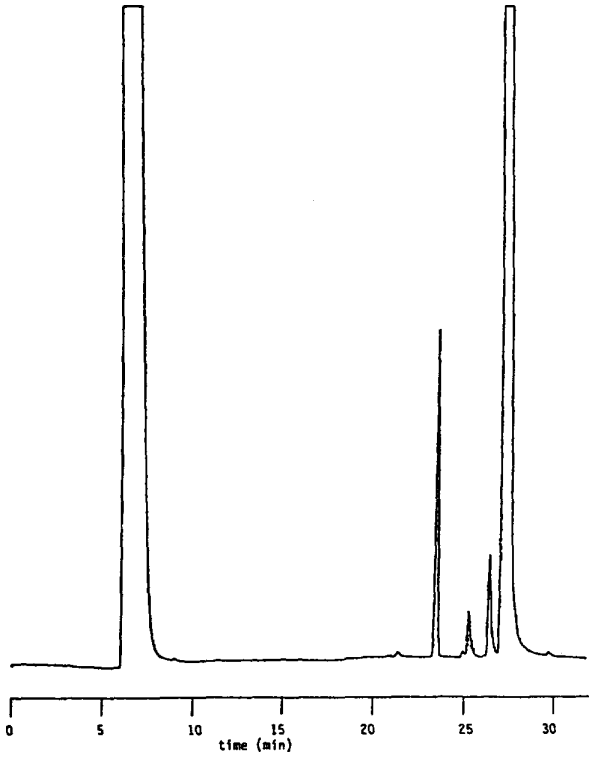


Fig. 29.

Supercritical Fluid Chromatogram of Occidental Crude CMPO Obtained with FID. Experimental conditions: 50 μm ID x 10 m length SB-methyl-100 column. Density program from 0.25 to 0.55 g/mL, ramped at 0.01 g/mL/min. Oven temperature at 110°C.

As indicated by the detector's name, compounds that are not detected by the NPD do not contain any nitrogen or phosphorus. When a compound contains both phosphorus and nitrogen atom, the peak intensity is enhanced in the NPD. Both NPD and FID are destructive detectors that are mass-flow-rate dependent and can be used for quantitative analysis. Both detectors have given information on which impurities in the CMPO contain N and/or P, but, in general, they are not considered to be useful for obtaining information on the chemical structure of compounds.

2. Mass Spectrometer (MS)

The SFC-MS is a powerful tool for both quantitative and qualitative analysis. Figure 30 is a chromatogram of purified CMPO from its analysis by SFC-MS. A CMPO peak appears at a retention time of 40 min. The mass spectrum from this SFC-MS analysis (Fig. 31) contains similar fragments as obtained from GC-MS [GATRONE].

Work is continuing in developing SFC-MS to identify impurities and degradation products of CMPO and TRUEX solvents.

3. Ultraviolet (UV) Detector

Figures 32 and 33 are chromatograms that were obtained in parallel from an analysis of crude CMPO by an FID and UV detector. The FID and UV detectors were placed in parallel using a T-shape splitter at the end of the column. The UV absorbance wavelength was set at 222 nm, which was determined to have the most sensitivity for CMPO and its impurities.

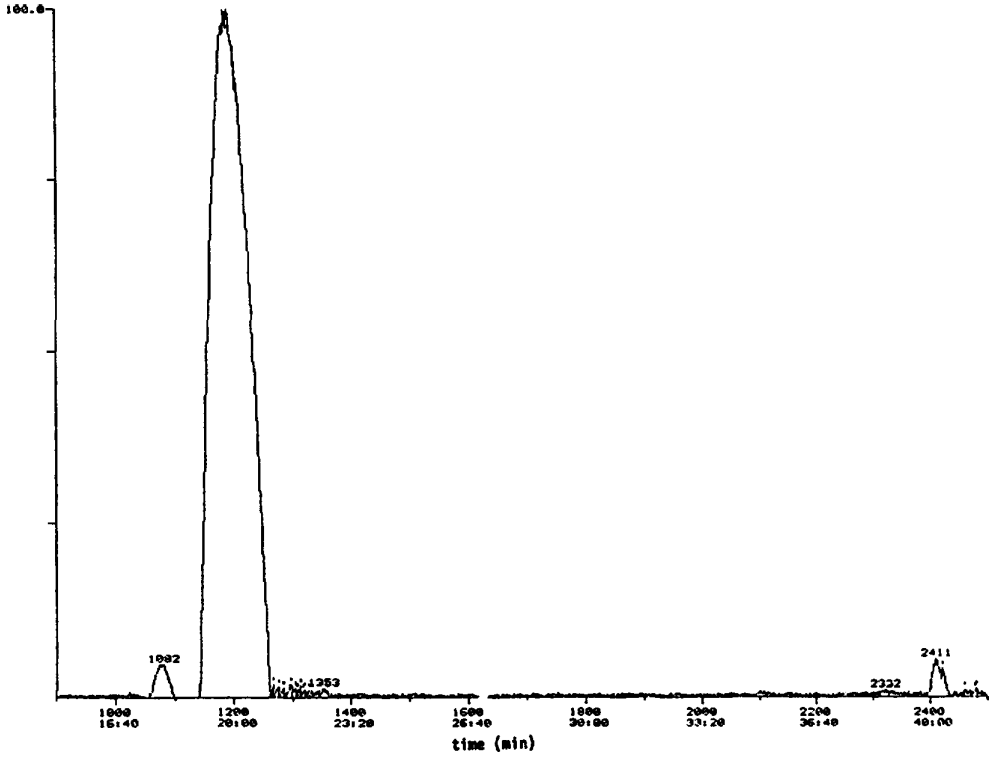


Fig. 30. Chromatogram from SFC-MS of CMPO. Experimental conditions: 50 μm ID x 10 m length SB-methyl-100 column. Density program from 0.25 to 0.55 g/mL, ramped at 0.01 g/mL/min. Oven temperature at 110°C.

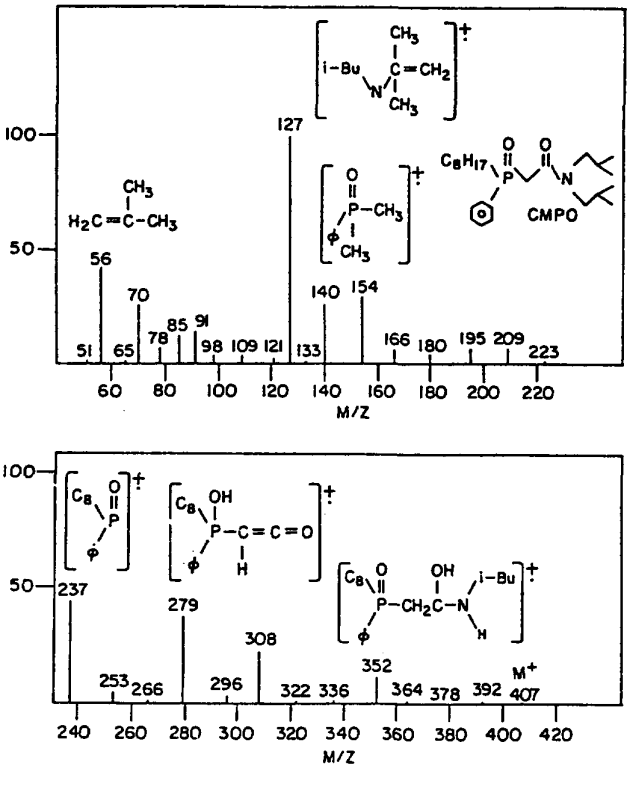


Fig. 31.

Chemical Ionization Mass Spectrum of CMPO from SFC/MS Analysis. (See Fig. 30 for Conditions.)

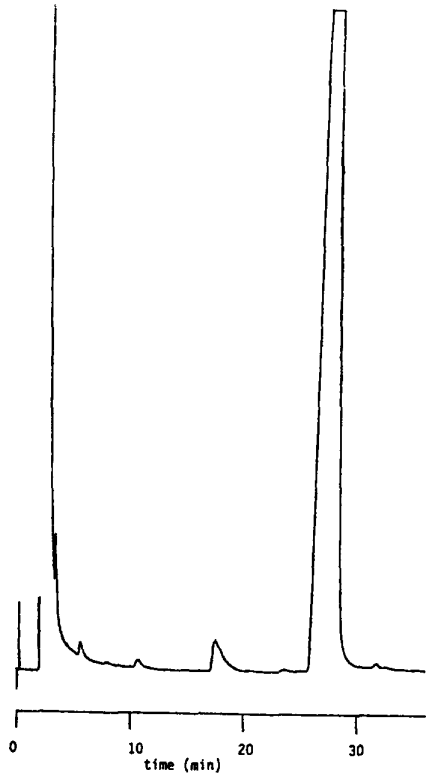
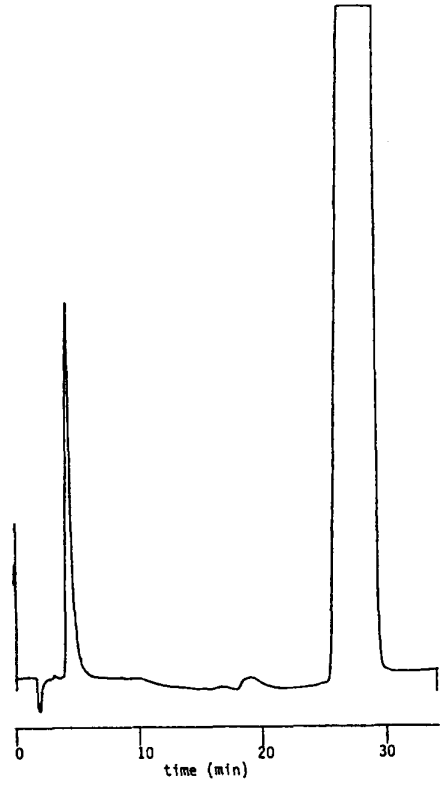


Fig. 32.

The SFC-FID Chromatogram of Crude CMPO Measured with Dual FID/UV Detectors. Experimental conditions: 50 μm ID x 10 m length SB-methyl-100 column. Density program from 0.25 to 0.55 g/mL, ramped at 0.01 g/mL/min. Oven temperature at 110°C.

Fig. 33.

The SFC-UV Chromatogram of Crude CMPO Measured with Dual FID/UV Detectors at 222 nm Wavelength. Experimental conditions: 50 μm ID x 10 m length SB-methyl-100 column. Density program from 0.25 to 0.55 g/mL, ramped at 0.01 g/mL/min. Oven temperature at 110°C.



Running two detectors simultaneously has the advantage of gaining additional information on the sample being analyzed. However, comparing Fig. 32 to Fig. 12 (obtained with the FID alone) shows the loss in resolution caused by splitting. The linear flow rate of the carrier fluid must be higher in the dual detector system than that with one detector. Part of the loss in the chromatographic resolution is caused by this higher flow rate. There is another important problem, the column butt connector. It is very difficult to line up two restrictors perfectly with the end of the column. In general, the column-restrictor interface is the cause of most chromatographic problems encountered in SFC capillary chromatography.

A comparison of the FID chromatogram (Fig. 32) to the UV chromatogram (Fig. 33) shows that they contain similar peak patterns. It, therefore, appears that many of these compounds are UV-active chromophores.

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We would also like to acknowledge the helpful discussions with Ralph Gatrone, E. Philip Horwitz, and Kenneth Nash, Chemistry Division, Argonne National Laboratory, where we compared data and experiences on the GC technique that they have developed for CMPO and TRUEX solvent analysis and this SFC technique. They also provided samples for our analyses.

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APPENDIX A
Standard Analysis of CMPO

The analysis of the CMPO consists of three parts: (1) sample preparation, (2) SFC analysis, and (3) calculation of results. Each of these parts will be discussed separately below.

Sample Preparation

A representative sample of the CMPO sample to be analyzed must be dissolved in dichloromethane (HPLC or GC grade) for injection into the SFC. Typically, ~10 mg of the sample would be weighed to an accuracy of 0.1 mg, placed in a 10 mL volumetric flask with ~2 mg of the C-24 standard (weighed to an accuracy of 0.02 mg), and diluted to the mark with dichloromethane.

SFC Analysis

A 100 μL syringe is used to inject ~50 μL of sample into the injection valve of the SFC. At least three replicate injections for each sample are recommended for accurate results. The equipment used in this study and, therefore, recommended for these analyses is a Lee Scientific Model 622 supercritical-fluid/gas chromatograph with a flame ionization detector (FID). A Spectra Physics SP4290 Integrator was used for peak-area analysis. Experimental parameters were:

- A 50 μm ID frit restrictor to control the column flow rate
- SFC-grade CO_2 (Scott Speciality Gas) as the carrier fluid
- Injection at room temperature
- Injector split ratio at 20 to 1
- Injection loop - 0.5 μL
- Oven temperature - 110°C
- Program - variable density, 0.25-0.6 g/mL, ramped at 0.01 g/mL/min
- Detector temperature - 325°C
- Column - 50 μm ID x 10 m length Lee Scientific superbond capillary SB-Methyl-100

The system must be calibrated to obtain a response factor for CMPO for use in calculating its purity. Appendix E describes the method used in this study and is an example of how this calibration can be done.

Calculation of Results

The calibration described in Appendix E is used to calculate a response factor (f) for CMPO in terms of the C-24 standard. The response factor for CMPO is:

$$f = \frac{\text{Mass(CMPO)/Mass(C-24)}}{\text{Peak Area(CMPO)/Peak Area(C-24)}}$$

The peak areas from the replicate SFC analyses are averaged, and the mass of CMPO in the sample is calculated from the peak-area ratio of CMPO to C-24 standard and the mass of C-24 in the sample. The percent purity of CMPO in the CMPO sample is 100 times the ratio of the mass of CMPO determined in the SFC analysis to that dissolved in the dichloromethane solution.

APPENDIX B
Standard Analysis of CMPO Dissolved in TBP

For ease of shipment and solvent preparation, it is likely that CMPO will be commercially available dissolved in TBP, typically at a TBP/CMPO mole ratio of greater than two. The analysis of the CMPO/TBP solution consists of three parts: (1) sample preparation, (2) SFC analysis, and (3) calculation of results. Each of these parts will be discussed separately below.

Sample Preparation

A representative sample of the CMPO/TBP sample to be analyzed must be dissolved in dichloromethane (HPLC or GC grade) for injection into the SFC. Typically, ~20 mg of the sample would be weighed to an accuracy of 0.2 mg, placed in a 10 mL volumetric flask with ~2 mg of the C-24 standard (weighed to an accuracy of 0.02 mg), and diluted to the mark with dichloromethane.

SFC Analysis

A 100 μL syringe is used to inject ~50 μL of sample into the injection valve of the SFC. At least three replicate injections for each sample are recommended for accurate results. The equipment used in this study and, therefore, recommended for these analyses is a Lee Scientific Model 622 supercritical-fluid/gas chromatograph with a flame ionization detector (FID). A Spectra Physics SP4290 Integrator was used for peak-area analysis. Experimental parameters were:

- A 50 μm ID frit restrictor to control the column flow rate
- SFC-grade CO_2 (Scott Speciality Gas) as the carrier fluid
- Injection at room temperature
- Injector split ratio at 20 to 1
- Injection loop - 0.5 μL
- Oven temperature - 110°C
- Program - variable density, 0.25-0.6 g/mL, ramped at 0.01 g/mL/min
- Detector temperature - 325°C
- Column - 50 μm ID x 10 m length Lee Scientific superbond capillary SB-Methyl-100

The system must be calibrated to obtain response factors for CMPO and TBP for use in calculating their purities and the composition of the mix. Appendix E describes the calibration method used in this study and is an example of how this calibration can be done.

Calculation of Results

The calibration described in Appendix E is used to calculate response factors (f) for CMPO and TBP in terms of the C-24 standard. The response factor for CMPO is:

$$f = \frac{\text{Mass(CMPO)/Mass(C-24)}}{\text{Peak Area(CMPO)/Peak Area(C-24)}}$$

There is an analogous response factor for TBP. The peak areas from the replicate SFC analyses are averaged for each component, and the masses of CMPO and TBP in the sample are calculated from the peak-area ratios of CMPO and TBP to C-24 standard and the mass of C-24 in the sample. The composition of the CMPO/TBP mix can be calculated from the mass of CMPO and the mass of TBP determined from the SFC analysis and that of the weighed CMPO/TBP in the sample-preparation step.

APPENDIX C
Standard Analysis for TRUEX-TCE Solvent

The analysis of the TRUEX-TCE solvent consists of three parts: (1) sample preparation, (2) SFC analysis, and (3) calculation of results. Each of these parts will be discussed separately below.

Sample Preparation

Before a sample can be injected into the SFC, it must be cleansed of metallic and acidic species that have been extracted into it during processing. The following procedures are conservative and may likely be streamlined once each procedure has been fully developed.

A. Solvent Known to Contain only Water-Soluble Acids

The procedure is simply:

1. A sample (~2 mL) of the solvent should be mixed (preferably using a vortex mixer) for about one minute with ~6 mL of deionized water in an appropriately sized glass culture or centrifuge tube. (The cap must be Teflon-lined; the solvent easily dissolves most plastics.) After centrifugation, the aqueous layer should be separated from the more dense organic phase, discarded, and replaced with fresh water. The procedure should be continued through three contacts.

2. After separation from the final water rinse, the sample should be contacted with ~8 mL of a 0.25M Na_2CO_3 solution for about one minute. As with the water wash, each of three contacts of the solvent with fresh aqueous solutions is followed by discarding the aqueous solution.

3. Step 1 should be repeated.

B. Solvent Believed to Contain Metallic Species

A more complicated procedure is necessary to treat these samples*:

1. A sample (~2 mL) of the solvent should be contacted (as described in step 1 of the first procedure) three times with three times its volume of an aqueous solution containing 0.05M oxalic acid and 0.5M HNO_3.

2. The solvent is next given three successive equal-volume contacts with an aqueous solution of 5M HNO_3, with the aqueous solutions being discarded after each has contacted the organic phase.

3. Steps 1-3 of the procedure described for acid-only solvent should be followed.

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*A less time-consuming and more reliable method using a powerful aqueous-phase complexant has been developed and tested for this procedure but can not be discussed due to patent concerns.

SFC Analysis

After the sample has been cleansed of acidic and metallic constituents, an aliquot should be measured by weight (~30 mg, measured to the nearest 0.2 mg) or by volume (~20 μL, measured by a micropipette with an accuracy of 0.2%) and delivered to a 10 mL volumetric flask. A known weight (~2 mg, measured to the nearest 0.02 mg) of the C-24 normal alkane standard should also be added to the flask. The sample is then diluted to the mark with dichloromethane (HPLC or GC grade) and mixed thoroughly.

A 100 μL syringe is used to inject ~50 μL of sample into the injection valve of the SFC. At least three replicate injections for each sample are recommended for accurate results. The equipment used in this study and, therefore, recommended for these analyses is a Lee Scientific Model 622 supercritical-fluid/gas chromatograph with a flame ionization detector (FID). A Spectra Physics SP4290 Integrator was used for peak area analysis. Experimental parameters were:

- A 50 μm ID frit restrictor to control the column flow rate
- SFC-grade CO_2 (Scott Speciality Gas) as the carrier fluid
- Injection at room temperature
- Injector split ratio at 20 to 1
- Injection loop - 0.5 μL
- Oven temperature - 110°C
- Program - variable density, 0.25-0.6 g/mL, ramped at 0.01 g/mL/min
- Detector temperature - 325°C
- Column - 50 μm ID x 10 m length Lee Scientific superbond capillary SB-Methyl-100

The system must be calibrated to obtain response factors for CMPO and TBP for use in calculating the concentrations in the solvent. Appendix E describes the method used in this study and is an example of how this calibration can be done.

Calculation of Results

The calibration described in Appendix E is used to calculate a response factor (f) for each component in terms of the C-24 standard. The response factor for CMPO is:

$$f = \frac{\text{Mass(CMPO)/Mass(C-24)}}{\text{Peak Area(CMPO)/Peak Area(C-24)}}$$

That for TBP, or any component, has a similar form. The peak areas from the replicate SFC analyses are averaged for each component, and the masses of CMPO and TBP in the sample are calculated from the peak-area ratios of each component to the C-24 standard and the mass of C-24 injected into the SFC. The concentrations (g/L) of CMPO and TBP in the solvent are then calculated from the concentration (g/L) of C-24 in the injected sample and the dilution of the solvent by the dichloromethane during preparation. Molar concentrations of components can then be calculated using the molecular weights (MW_{CMPO} = 407.58 g/mol, MW_{TBP} = 266.32 g/mol).

APPENDIX D
Standard Analysis of the TRUEX-NPH Solvent

The analysis of the TRUEX-NPH solvent consists of three parts: (1) sample preparation, (2) SFC analysis, and (3) calculation of results. Each of these parts will be discussed separately below. The analysis is identical to that for the TRUEX-TCE solvent except that (1) the organic phase is the less dense phase in the contacts with aqueous solutions during sample preparation, and (2) the chromatograms are complicated by the peaks associated with the components of the mixed NPH diluent. The $C_{10}H_{24}$ through $C_{15}H_{24}$ components of the C_{12}-C_{14} NPH mixture fall between the dichloromethane and the TBP peaks and do not interfere with measurements of either the TBP or the CMPO peaks.

Sample Preparation

Before a sample can be injected into the SFC, it must be cleansed of metallic and acidic species that have been extracted into it during processing. The following procedures are conservative and may likely be streamlined once each procedure has been fully developed.

A. Solvent Known to Contain Only Water-Soluble Acids

The procedure is simply:

1. A sample (~2 mL) of the solvent should be mixed (preferably using a vortex mixer) for about one minute with ~6 mL of deionized water in an appropriately sized glass culture or centrifuge tube. (The cap must be Teflon-lined; the solvent easily dissolves most plastics.) After centrifugation, the aqueous layer should be separated from the less dense organic phase, discarded, and replaced with fresh water. The procedure should be continued through three contacts.

2. After separation from the final water rinse, the sample should be contacted with ~8 mL of a 0.25M Na_2CO_3 solution for about one minute. As with the water wash, each of three contacts of the solvent with fresh aqueous solutions is followed by discarding the aqueous solution.

3. Step 1 should be repeated.

B. Solvent Believed to Contain Metallic Species

A more complicated procedure is necessary to treat these samples*:

1. A sample (~2 mL) of the solvent should be contacted (as described in step 1 of the first procedure) three times with three times its volume of an aqueous solution containing 0.05M oxalic acid and 0.5M HNO_3.

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*A less time-consuming and more reliable method using a powerful aqueous-phase complexant has been developed and tested for this procedure but can not be discussed due to patent concerns.

2. The solvent is next given three successive equal-volume contacts with an aqueous solution of 5M HNO_3, with the aqueous solutions being discarded after each has contacted the organic phase.

3. Steps 1-3 of the procedure described for acid-only solvent should be followed.

SFC Analysis

After the sample has been cleaned of acidic and metallic constituents, an aliquot should be measured by weight (~30 mg, measured to the nearest 0.2 mg) or by volume (~20 μL, measured by a micropipette with an accuracy of 0.2%) and delivered to a 10 mL volumetric flask. A known weight (~2 mg, measured to the nearest 0.02 mg) of the C-24 normal alkane standard should also be added to the flask. The sample is then diluted to the mark with dichloromethane (HPLC or GC grade) and mixed thoroughly.

A 100 μL syringe is used to inject ~50 μL of sample into the injection valve of the SFC. At least three replicate injections for each sample are recommended for accurate results. The equipment used in this study and, therefore, recommended for these analyses is a Lee Scientific Model 622 supercritical-fluid/gas chromatograph with a flame ionization detector (FID). A Spectra Physics SP4290 Integrator was used for peak area analysis. Experimental parameters were:

- A 50 μm ID frit restrictor to control the column flow rate
- SFC-grade CO_2 (Scott Speciality Gas) as the carrier fluid
- Injection at room temperature
- Injector split ratio at 20 to 1
- Injection loop - 0.5 μL
- Oven temperature - 110°C
- Program - variable density, 0.25-0.6 g/mL, ramped at 0.01 g/mL/min
- Detector temperature - 325°C
- Column - 50 μm ID x 10 m length Lee Scientific superbond capillary SB-Methyl-100

The system must be calibrated to obtain response factors for CMPO and TBP for use in calculating the concentrations in the solvent. Appendix E describes the method used in this study and is an example of how this calibration can be done.

Calculation of Results

The calibration described in Appendix E is used to calculate a response factor (f) for each component in terms of the C-24 standard. The response factor for CMPO is:

$$f = \frac{\text{Mass(CMPO)/Mass(C-24)}}{\text{Peak Area(CMPO)/Peak Area(C-24)}}$$

That for TBP, or any component, has a similar form. The peak areas from the replicate SFC analyses are averaged for each component, and the masses of CMPO and TBP in the sample are calculated from the peak-area ratios of each component to the C-24 standard and the mass of C-24 injected into the SFC. The concentrations (g/L) of CMPO and TBP in the solvent are then calculated from the concentration (g/L) of C-24 in the injected sample and the dilution of the solvent by the dichloromethane during preparation. Molar concentrations of components can then be calculated using the molecular weights (MW_{CMPO} = 407.58 g/mol, MW_{TBP} = 266.32 g/mol).

APPENDIX E
Calibration of System for CMPO and TBP SFC Analysis

Accurately quantitating the amounts of CMPO and TBP in various samples is highly dependent on the accuracy of this calibration. Special care must be given to using the purest obtainable forms of CMPO and TBP. The TBP used in our studies was Aldrich gold label (99+% pure). The CMPO used for this calibration was commercially available SX-grade that had gone through the purification method described in the body of this report three successive times; the purity of this material is likewise believed to be 99+% pure. The C-24 standard was purchased from Chem. Service, Inc. as 99% pure. Calibration consists of three distinct parts: solution preparation, SFC analysis, and calculation. Each of these parts will be discussed separately below.

Solution Preparation

A series of at least six solutions should be prepared where the concentration of CMPO is varied over a range of at least 50. These solutions may also contain TBP that is varied over an equivalent concentration range. The molar ratio of CMPO to TBP has been found to have an unmeasurable effect on the response factor for these two species over a range of 1/2 to 1/8, but it is always prudent to make this ratio close to that which is expected in the samples to be analyzed. Individual solutions may be prepared by weighing specific amounts of CMPO and TBP and diluting to the mark of a volumetric flask with dichloromethane, or by undertaking serial dilutions from at least two concentrated stock solutions. In any case, errors associated with weighings and volume transfer should be kept to 0.1%. A convenient CMPO concentration range for the calibration is between 0.01 and 0.5 mg/mL. A carefully administered amount of the C-24 standard (~0.2 mg/mL, again known to an accuracy of 0.1%) should also be added to each standard solution. The diluent (TCE or NPH) may also be added to these solutions in concentrations appropriate to the samples being analyzed.

SFC Analysis

A 100 μL syringe is used to inject ~50 μL of solution into the injection valve of the SFC. At least five replicate injections for each solution are recommended for accurate results. The equipment used in this study and, therefore, recommended for these analyses is a Lee Scientific Model 622 supercritical-fluid/gas chromatograph with a flame ionization detector (FID). A Spectra Physics SP4290 Integrator was used for peak-area analysis. Experimental parameters were:

- A 50 μm ID frit to control the column flow rate
- SFC-grade CO_2 (Scott Speciality Gas) as the carrier fluid
- Injection at room temperature
- Injector split ratio at 20 to 1
- Injection loop - 0.5 μL

- Oven temperature - 110°C
- Program - variable density, 0.25-0.6 g/mL, ramped at 0.01 g/mL/min
- Detector temperature - 325°C
- Column - 50 μm ID, 10 m length Lee Scientific superbond capillary SB-Methyl-100

Calculation of Results

The peak areas for each component from replicate analyses should be averaged, and the averaged peak areas for each component will be used to calculate a response factor (f) in terms of the peak area for the C-24 internal standard. A plot of the ratio (mass of CMPO/ mass of C-24) vs. the ratio (peak area of CMPO/peak area of C-24) will produce a straight line with the slope equal to f; i.e., the response factor for CMPO is:

$$f = \frac{\text{Mass(CMPO)/Mass(C-24)}}{\text{Peak Area(CMPO)/Peak Area(C-24)}}$$

There is an analogous response factor for TBP and other components.

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