

SPECIFIC METAL DETECTION IN THE SIZE EXCLUSION SEPARATION
OF SEPARATION OF SOLVENT REFINED COAL

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INTRODUCTION

The high sensitivity of Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) for metal analysis(2) makes this system a potentially powerful metal-specific detector for liquid chromatographic separations. Several reports have recently appeared regarding a chromatography-ICP interface(3). Practically all of these investigations have involved an aqueous mode where the characteristics of the plasma are much better understood(2).

Exceptions to this are the simultaneous determination of 15 different wear metals in lubricating oils dissolved in 4-methyl-2-pentanone(4) and the separation with toluene eluent of a test mixture of ferrocene compounds via adsorption chromatography with ICP-AES as a single element detector(5). The extension of LC-ICP to a variety of organic solvents wherein organometallic compounds are more compatible has not been made. To accomplish this task one requires an efficient interface which can handle a variety of solvents with their accompanying differences in nebulization efficiencies since the plasma is extremely sensitive to changes in solvent delivery, solvent composition and solvent volatility. A change of solvent can lead to changes in background emissions, coupling of the radio frequency to the plasma and differences in optimal viewing height of the plasma. A jacketed spray chamber whereby coolant can flow or be pumped around the exterior proved to be the choice interface(6). Metal detection limits in such solvents as pyridine, chloroform, toluene and heptane have been shown to be comparable to those found in aqueous static ICP-AES operation.

Pyridine has a number of features as a solvent that makes it interesting for development both as a LC solvent and a solvent for ICP-AES. Pyridine is particularly desirable for most all synfuel materials in that it dissolves, for example, approximately 98% of solvent refined coal solid product. In addition, we have shown it to be an acceptable solvent for size exclusion chromatography (SEC) of coal derived products(7). The results of the SEC separation in pyridine of a variety of coal derived fractions utilizing ICP as a specific metal detector are described herein.

EXPERIMENTAL

An ARL (Sunland, CA) ICP-AES Model 137000 was used as obtained for metal detection. The software utilized was significantly modified from that which is commercially available and can be obtained from the authors. The argon gas flows for the nebulizer and coolant were as delivered when setting the regulators at 15 and 40 psi, respectively. The system, including torch position, was optimized for pyridine. Pyridine was purchased as a chromatographic grade solvent with no special precautions as to metal content. The pumping system for the chromatographic separations was a Waters 6000A dual piston pump (Milford, MA). The separations were achieved using a 100Å μ -Styragel column (Waters, Milford, MA) at a flow rate of either 1 or 0.5 ml/min.

All tubing between the sample injection valve (Valco, 50 μ l loop) and the nebulizer was fabricated from either 316 stainless steel or Teflon. The nebulizer,

composed of Pyrex glass, was obtained from ARL. A thermostated Pyrex glass spray chamber, developed in this laboratory, to facilitate the interface and also be compatible with volatile organic solvents was utilized. The plasma was maintained at 1400 watts incident power and zero watts reflected power.

Separation of solvent refined coal by selective elution solvent chromatography (SESC) (8) was carried out by slurring approximately 200 grams of silica gel (70-230 mesh) (MC/B Manufacturing Chemists Inc.) in one liter of dry methanol and filtering through a Whatman #1 cellulose filter. The silica gel was further washed with three 200 ml of volumes of methanol and dried at 120°C in a gravity convection oven. The chromatographic column was a 1 3/4 inch o.d. x 10 inch long stainless steel tube with fritted reducers that lead to 1/16 inch o.d. tubing outlets. To gravity pack the column, approximately 130 grams of the prepared silica gel was slurried in 500 ml of HPLC grade hexane and poured into the chromatographic column. Once drained of hexane, a sample mixture of SRC and silica gel (1:1) was dry packed onto the column head. The solvents used for the chromatography were those previously reported (8). Having isolated the nine SESC fractions, each was individually reduced in volume through rotary evaporation at 40°C (60°C for pyridine) under vacuum. Each fraction was further dried at 60°C and 5 torr for 24 hours.

For size exclusion chromatography, these SESC fractions were redissolved in pyridine at approximately 0.5 grams of fraction to 10 milliliters of solvent. The solutions were filtered through 0.45 micrometer Millipore syringe filters. Fifty microliters of each of the resulting solutions was then injected on a 100A μ -Styragel column and eluted with pyridine.

RESULTS AND DISCUSSION

We have developed a LC-ICP interface which can simultaneously detect (ICP) and speciate (LC) up to 34 elements at concentrations between 10 ppm and 0.5 ppb depending on the element and the matrix. A variety of organic matrices have been successfully used. Preliminary experiments using this interface have monitored 15 elements simultaneously (Al, Ca, Cd, Co, Cr, Cu, Fe, Hg, Mg, Mn, Mo, Ni, Ti, V and Zn). The mode of separation of process derived coal liquefaction solvents and Amax solvent refined coal has been size exclusion chromatography.

The metals present in a process solvent obtained from the SRC Wilsonville, AL facility and metal distribution according to effective molecular size are presented in Figure 1. Very low levels of Mg, Mn, Ti, Cd and Hg are observed. A rather broad molecular size distribution is found for Mg; whereas, Ti appears to be more mono-dispersed with an average molecular size via retention volume approximately equivalent to a 500 molecular weight n-alkane. A definite bimodal distribution is observable for Mn. Of the elements which were monitored, Cr surprisingly exhibits the largest concentration unlike the other coal-derived materials which have been examined via LC-ICP. The source of Cr in this case may well be from corrosion of the reactor equipment. Both Cr and Fe show a similar molecular size distribution with most of the material eluting near the totally excluded volume. Cu and Zn, on the other hand, show a much smaller size distribution with Cu having at least two groups of "sized" species; while, Zn appears to be incorporated in a relatively small number of single "sized" species. The remainder of the elements monitored did not show detectable peaks above ambient noise level.

A moderately hydrotreated process solvent that had been previously separated into four distillation ranges: IBP (initial boiling point) -800°F, 400-800°F, 400-600°F and 600-800°F was subjected to SEC-ICP. Figure 2 shows three such distillation cuts

separated on a 100Å μ -Styragel SEC column using pyridine as the eluting medium. Since the 400-600°F and the 600-800°F fractions were taken from the ICP-800°F distillate, one would hope that these should be additive. Indeed, if one looks at the Fe "metallogram" of the 400-600°F cut, one sees a distribution that is bimodal with the predominant fraction being of smaller molecular size, while the 600-800°F Fe metallogram is likewise bimodal but the predominant fraction being of larger molecular size. The original IBP-800°F distillate also appears to be bimodal but with equal distribution of smaller and larger molecular sized compounds. It is also satisfying that the higher temperature range distillate exhibits an increased concentration of larger (less volatile) compounds.

Zn appears to be concentrated in the lower temperature distillate. The higher temperature distillate has smaller sized Zn compounds although the reason is not clear. This may imply that these Zn containing species are more polar and hence more highly associated. No detectable levels of Mn were observed in the SEC of both the 400-600°F and 600-800°F cut. The IBP-800°F cut, however, showed a low Mn lost in the distillation or severely diluted as a result of the distillation. On the other hand, Cu is retained upon distillation and is equally divided between the two more narrow boiling cuts. Of the 15 elements monitored, only the metals shown in Figure 2 were above the minimum detectable limit.

ICP alone will not yield speciation information; coupled, however, with specific types of chromatography some knowledge of the nature of metal species can be obtained. A preparative separation of SRC solid product via polarity on silica gel has been performed employing selected elution solvent chromatography (SESC) into nine fractions, designated saturates (#1), aromatics (#2), polar aromatics (#3), simple phenols (#4), nitrogen heterocycles (#5), highly functional molecules (#6), polyphenols (#7), and molecules that possess increasing oxygen and nitrogen content (#8 and #9). We found significant quantities of a variety of metals in each SESC fraction (9). After removing the eluting solvent, we separated each SESC fraction further according to effective molecular size by elution with pyridine with the ICP "on-line" to obtain fifteen "metallograms", one for each metal and SESC fraction monitored.

Copper, iron and zinc metallograms show the richest variety of metallic species detected (Figure 3). All nine SESC fractions contain varying amounts of these metals. SESC #1 and #8 have the highest concentration of copper; SESC #1 and #6 have the highest concentration of iron; and SESC #8 has, by far, the highest concentration of zinc. The multiple chromatographic peaks registered in most metallograms testify to the wide variety of organically bound copper, iron and zinc species in the SRC studied. The sharpness of many of the peaks, especially in the case of zinc, suggests exclusive elution of closely related components or even of just a single species. Elution of iron species commences at the totally excluded volume for each SESC fraction. This is not the case with copper and zinc; for these metals, molecules of size less than an n-C₁₀ alkane are predicted to elute. Iron-containing materials eluting in highly polar SESC fractions are large "sized" entities, while a much broader "sized" distribution is observed in less polar fractions (SESC #1-6). Major copper and zinc peaks eluting from SESC #1 correspond to approximately 1.3 ppm (Cu) and 0.4 ppm (Zn). Other relatively sharp peaks where concentration can be estimated are provided in the copper metallogram derived from SESC #7. Progressing to smaller "sized" species (increasing elution volume) the copper concentrations are approximately 0.8, 2.3 and 1.1 ppm, respectively. Since SESC #7 is reputed to be polyphenols, it seems reasonable to suggest that these copper signals are due to elution of copper phenolates. The zinc metallogram derived from SESC #6 exhibits the largest number of discrete peaks. Four zinc containing species in this highly functional fraction are revealed upon separation by effective molecular size. The

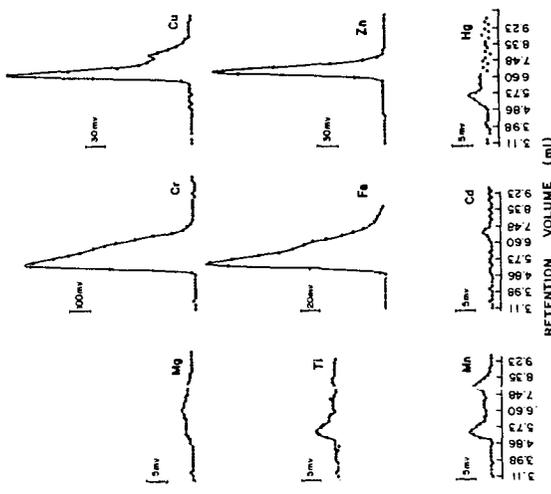
apparent largest "sized" zinc compound elutes at the totally excluded volume and represents approximately 6 ppm zinc. Elution of the species at 10.5 ml is representative of a molecule corresponding to n-decane in size. SESC #8 has a zinc concentration of about 45 ppm, all of which apparently elutes in a relatively narrow band corresponding in size to an n-C₂₄ alkane. Finally, an interesting bimodal separation of totally excluded and selectively permeated (~0.25 ppm) zinc-containing material is observed in the size exclusion separation of SESC #9.

A capability to perform metal analyses in pyridine and other organic solvents and the interfacing of LC and ICP provide researchers a tool for metal speciation in synfuels. Further work must be undertaken to ascertain specific chemical environments of each metal. However, solubility of these materials in a wide variety of organic solvents, repeated filtration through 5µm filters, and selective separation via two chromatographic procedures (SESC and SEC) indicates that metals in organic combination are present(10).

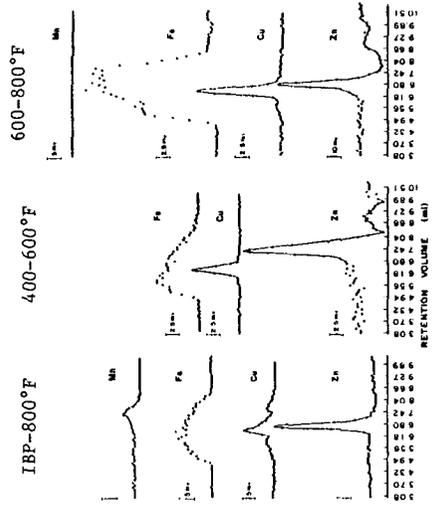
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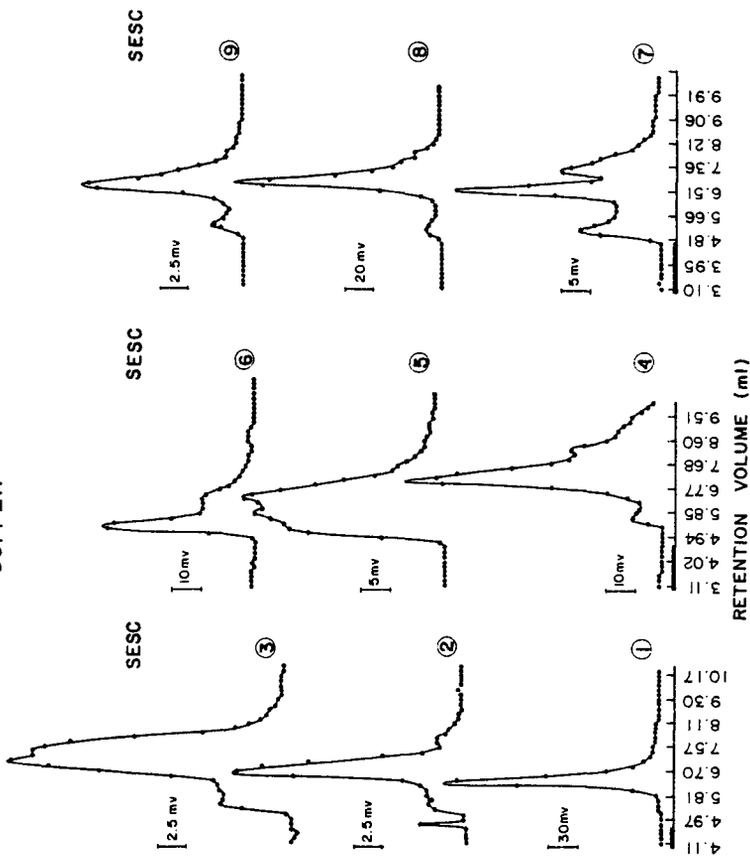
Size Exclusion Chromatographic Metallogram of Wilsonville Process Solvent employing specific metal detection and pyridine elution.



Size Exclusion Chromatographic metallogram of hydrotreated process solvent employing specific metal detection and pyridine elution

FIGURE 2

COPPER



Size Exclusion Chromatographic metallogram of nine SESC fractions employing pyridine elution and Cu detection

FIGURE 3A

