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LANTHANIDE METAL CHELATES AS SELECTIVE COMPLEXING SORBENTS FOR GAS CHROMATOGRAPHY

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SUMMARY

Stationary phases containing β -diketonate chelates of the lanthanides can be used as pre-analytical columns to retain selectively and separate nucleophilic species from non-nucleophilic species by metal complex formation. The ability of the chelates to accept additional donor atoms in the coordination sphere of the lanthanide and to form strong complexes with oxygen-containing compounds causes enhanced retention of the oxygenates in the pre-column. Compounds which do not form complexes or form only very weakly bonded complexes (*e.g.*, alkanes, alkenes, aromatics, chlorinated compounds and sterically hindered nucleophiles) are eluted in a normal fashion and analyzed by the gas chromatograph. Subsequent heating of the pre-column dissociates the complexes; the nucleophiles (*e.g.*, aldehydes, ketones, esters, ethers, alcohols, etc.) are removed and analyzed as a separate fraction. The technique results in simplification of complex chromatograms as well as class-specific analysis.

INTRODUCTION

The ability of metal atoms to alter or to enhance chromatographic separations has been known for some time. The effect of compounds of Ag(I) on separations of unsaturated compounds is well documented and a review by Guha and Janák covers much of this work¹. In addition to silver-containing stationary phases, compounds of mercury(I) have been used either as subtractor columns or analytical columns in the gas chromatographic analysis of olefins^{2,3}. Subtractor columns of PdSO₄ have been used to remove oxygenated species from jet exhaust². Compounds of Cu(II) have been used to effect separations of aromatic amines^{4,5}. Chelates of nickel, zinc, cobalt, manganese and chromium have also been studied for their selectivity as sorbents⁶⁻⁸. Two recent review articles summarize the use of transition metal complex formation in gas chromatography^{9,10}.

Studies of chelates of the lanthanides have provided ample evidence of selectivity for various donor molecules. In the case of highly electron withdrawing beta-diketonate ligands, relative increases of up to eighty-fold in retention times were reported for strong donor molecules when the metal chelate was added to the liquid phase of a gas chromatographic column^{11,12}. The high selectivity available with these

compounds suggests their use as pre-analytical column sorbents for separation schemes prior to gas chromatographic analysis. We report here the synthesis of a sorbent based upon a novel lanthanide complex and its application to the separation of some complex mixtures.

EXPERIMENTAL

Apparatus

A dual sorbent sampling system was constructed and is illustrated in Fig. 1. Two multiport valves (Valco, Houston, TX, U.S.A.), one six-port and one four-port, were installed in a heated enclosure. A $10 \times 1/8$ in. O.D. stainless steel U-tube trap equipped with its own temperature controller and insulated jacket (Valco) was mounted on the valve box and connected to the six-port valve. This trap is used to hold the lanthanide sorbent. Two gas connections with toggle shut-off switches were also attached to the six-port valve. The first connection comes directly from either a flowmeter or pressure regulator (depending on whether packed or capillary columns are used) and contains pure carrier gas. The second connection comes from the regulator or meter but can be easily removed so that a glass trap containing a porous polymer can be inserted in this line. This glass trap can be heated to desorb compounds trapped on the porous polymer. The two remaining lines of the six-port valve are connected to the four-port valve, which directs flow either to vent or into the analytical column of the gas chromatograph. The entire assembly was mounted on a gas chromatograph and connected directly to the column using no injection port. The system

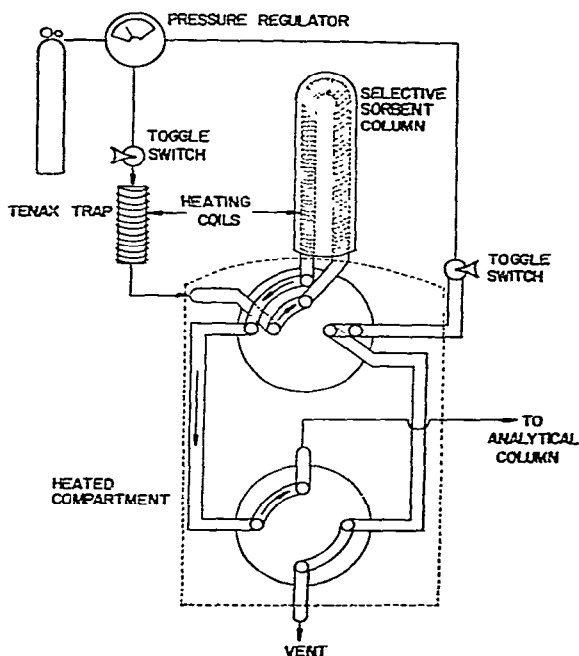


Fig. 1. Schematic of dual sorbent sample system that permits three modes of operation; analysis of total mixture, analysis of non-retained compounds, and analysis of retained compounds.

allows three basic modes of operation. Volatile compounds are trapped on a porous polymer [e.g., Tenax GC, poly(2,6-diphenyl-*p*-phenylene oxide)], and thermally desorbed directly into the gas chromatograph. A variety of techniques have been described previously¹³⁻¹⁵. This results in a chromatogram containing all the desorbed compounds, which is referred to in this paper as the total mixture.

In a different mode, an identical sample sorbed on the Tenax GC polymer can be desorbed into the lanthanide pre-column before entering into the chromatograph. Compounds eluting through the lanthanide pre-column are directed into the analytical column and trapped by thermal focusing. Upon temperature programming the analytical column, analysis of compounds that do not form stable complexes is performed.

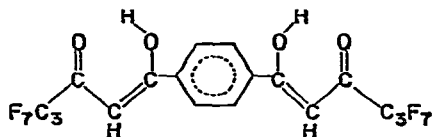
In the third mode the lanthanide column is heated and back-flushed with carrier gas to remove the retained compounds, which again are deposited on the cooled analytical column. Subsequently the analytical column is temperature programmed and nucleophilic compounds that form stable complexes are analyzed.

Gas chromatograph

Two columns were used in this study. A glass column (2 m × 2 mm I.D.) packed with 0.1% SP-1000 on Carboxpack C 80/100 was used for the less complex, more volatile mixtures. Later a 30-m fused silica capillary column coated with SE-52 (J & W Scientific, Orangevale, CA, U.S.A.) was used for the analysis of more complex mixtures. The capillary column was installed in either a Hewlett-Packard 5830 gas chromatograph or in a Hewlett-Packard GC/MS/DS 5982A modified by Dr. R. Barkley so that the silica column is connected directly to the ion source.

Synthesis of *p*-di(4,4,5,5,6,6,6-heptafluoro-1,3-hexanedionyl)benzene, H_2 dihed

A 2-l three-neck flask was fitted with a reflux condenser and a dropping funnel. A volume of 500 ml of dry ether was added to the flask along with 34.8 g (0.646 moles) of sodium methoxide and 74.5 g (0.308 moles) of ethyl heptafluorobutyrate. The mixture was stirred in ice bath at 0°C. Over the course of 45 min a slurry of 25 g (0.154 moles) of *p*-diacetylbenzene in 500 ml dry ether was added to the flask, resulting in a bright orange-yellow solution. The reaction was allowed to stir an additional 45 min. The mixture was then neutralized with 50% HCl (200 ml) to pH 1 and an additional 300 ml of water was added to the mixture. The ether layer was removed and evaporated to dryness with a rotary evaporator. The crude orange-yellow product was recrystallized three times from ethanol, yielding beige or light yellow flakes with a m.p. of 146–147°C; yield 52.9 g (62%). The structure of the ligand (MW = 554) is shown below. Confirmation of identity was obtained by electron impact mass spectrometry and proton nuclear magnetic resonance spectrometry (NMR).



H_2 dihed

An europium(III) complex of the ligand was synthesized. Three grams of ligand in 150 ml of MeOH were neutralized with 2.7 ml of 4 M NaOH and then slowly added to 1.1 g $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in 50 ml MeOH. The entire mixture was added dropwise to 300 ml of water. A light yellow solid (m.p. $>300^\circ\text{C}$ with decomp.) precipitated, which was slightly soluble in MeOH but insoluble in most other organic solvents. The elemental analysis of the complex was 29.73% C, 1.29% H and 36.88% F. An average molecular weight in methanol of 1411 was determined by vapor pressure osmometry. From these data a number of structures for the complex are possible, including a dimer with molecular formula $\text{Eu}_2(\text{dihed})_2(\text{OH})_2(\text{H}_2\text{O})_x$. The solid material may be a higher polymer which dissociates in methanol to lower molecular weight oligomers.

Preparation of lanthanide pre-column

An amount of 550 mg of the europium complex was dissolved in 100 ml methanol. This was added to a round-bottom flask containing a solution of 300 mg SE-30 polydimethylsiloxane in 200 ml chloroform. Ten grams of 80–100 mesh Gas-Chrom Z were added, the mixture was stirred and the solvent removed on a rotary evaporator. The packing material was allowed to dry in the open air overnight. No attempt was made to further remove solvent.

The packing material was packed into a stainless steel column and fitted with a plug of glass wool at both ends. Conditioning of the europium column at 220°C with carrier flow for 15 min was usually sufficient to achieve suitably low blanks.

Eu(fod)₃ on Porasil

Prior to synthesis of the europium complex, $[\text{Eu}(\text{dihed})]_x$, a preliminary study was undertaken to evaluate the ability of lanthanide chelates to perform pre-analytical column separations. A sorbent system similar to the one described, but less sophisticated and effective, was constructed and a sorbent material consisting of 0.5 g $\text{Eu}(\text{fod})_3$ (Hfod = 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedione), which is commercially available from Aldrich (Milwaukee, WI, U.S.A.), coated onto 10 g of Porasil C (Waters Assoc., Milford, MA, U.S.A.) was packed into a 5 cm \times 4 mm I.D. glass column. The $\text{Eu}(\text{fod})_3$ -Porasil column was conditioned at 150°C for 1.5 h prior to use.

RESULTS AND DISCUSSION

Preliminary tests with Eu(fod)₃-Porasil

Lanthanide(III) β -diketonates have been used extensively as nuclear magnetic resonance shift reagents^{16–18}. In particular, the lanthanide chelates of H(fod) are known to be especially effective for this application. The coordinatively unsaturated as well as hard Lewis acid nature of the lanthanide chelates enables them to form complexes with hard Lewis bases such as oxygen- and nitrogen-containing compounds. This selective formation of complexes with certain classes of compounds should have certain important applications in gas chromatography. Three applications of lanthanide chelate columns were investigated: solvent removal, removal of interferences, and class separations.

The $\text{Eu}(\text{fod})_3$ -Porasil sorbent was placed in the injection port of a gas chro-

matograph which was maintained at 170°C. An injection of 0.2 μl of a solution of 1 $\mu\text{g}/\mu\text{l}$ of decane, dodecane, tetradecane and hexadecane in methanol resulted in the complete removal of methanol from the chromatogram, while decane, dodecane and tetradecane were eluted quantitatively. The hexadecane was recovered in lower yield ($\sim 50\%$).

In order to recover completely tetradecane and remove completely the methanol solvent on the short pre-column, one must increase selectively the retention time of methanol such that it is greater than that of tetradecane. In this example it would be equivalent to approximately a 20-fold increase in retention time. Brooks and Sievers reported that alcohols do indeed form stable complexes with $\text{Eu}(\text{fod})_3$ and that the relative increases were in the range of from thirteen to twenty-two times that for the phase that does not contain $\text{Eu}(\text{fod})_3$ (ref. 12). The hexadecane, however, is not well separated from the methanol under these conditions due to its lower volatility. It is felt the utility of such a pre-column to remove solvent has applicability in the area of capillary columns where large excesses of solvent tend to degrade resolution. A disadvantage, however, might be the ability of the pre-column to remove oxygenated solutes as well as the solvent, though this may at times be desirable. One other application would be the ability to use non-water miscible polar solvents such as *n*-octanol as extraction solvents in analysis schemes followed by removal of the octanol by this method. Selective pre-columns of $\text{Cu}(\text{II})$ have been used to remove pyridine solvent from a mixture⁴.

The possibility of removing interferences in environmental samples is illustrated in Fig. 2. Shown above and below are chromatograms of the volatile components from a 100-ml sample of treated sewage effluent from the Boulder, Colorado, waste treatment facility. Both samples were purged into a Tenax trap, followed by thermal desorption into a gas chromatographic analytical column at 30°C. The upper trace shows the elution of the total mixture upon temperature programming, while the lower trace results when the compounds are passed through the $\text{Eu}(\text{fod})_3$ -Porasil pre-column which was maintained at 150°C. Identification of the compounds removed by the pre-column revealed that 2-propanol, acetone and tetrahydrofuran were removed, while methylene chloride, diethyl ether, chloroform, a heptane isomer and toluene were eluted through the pre-column.

The ether is not retained well by the column even though it is an oxygenated species and apparently forms a less stable complex than the sterically unencumbered tetrahydrofuran. Previous lanthanide shift reagent studies have shown that non-cyclic ethers as a class form only weak complexes¹⁹. An increased retention time of only four-fold was reported by Feibush *et al.*¹¹ for diethyl ether on a $\text{Eu}(\text{fod})_3$ -containing liquid phase. The cyclic ether tetrahydrofuran, however, was the most efficiently retained compound examined in that work, showing a increase of eighty-fold in retention time. This is illustrated here by its absence from the chromatogram of the mixture passed through the $\text{Eu}(\text{fod})_3$ pre-column even though high concentrations of tetrahydrofuran were initially present. Clearly, more serious interferences than shown here could be removed from chromatograms in the analysis of, for example, volatile halogenated pollutants.

The sorption of nucleophiles on the $\text{Eu}(\text{fod})_3$ -Porasil column is a reversible process for more volatile compounds. A mixture containing chloroform, cyclohexane, ethyl acetate, methyl isopropyl ketone and toluene was spiked into water at approxi-

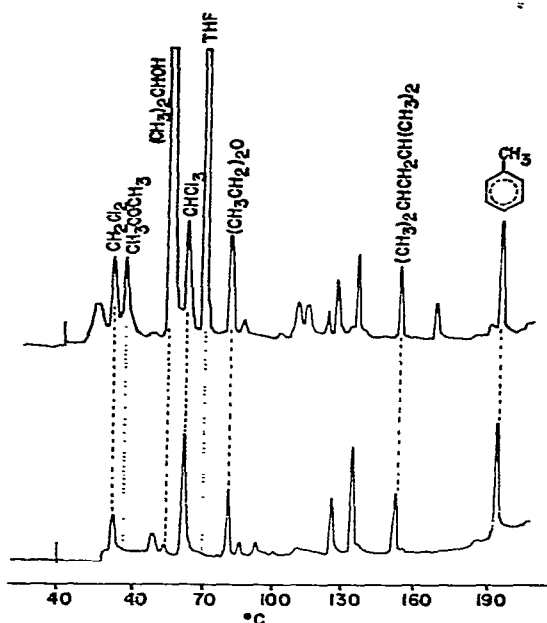


Fig. 2. Chromatograms of the volatile compounds in treated wastewater. The top trace is the total mixture. The bottom trace results when the volatiles are passed through $\text{Eu}(\text{fod})_3$ -Porasil to remove the complex-forming nucleophiles. Analytical column: 0.1% SP-1000 on Carbowack C 80/100. He flow-rate, 30 ml/min, temperature program, sorption on Carbowack column at ambient temperature, then heated at 40°C for 4 min, then from 40 to 190°C at $8^\circ/\text{min}$.

mately the 100-ppb level and purged into a Tenax trap. The compounds on Tenax were thermally desorbed into the cooled gas chromatographic analytical column and the total mixture analyzed.

A second identical sample was purged onto Tenax, and desorbed for 4 min; however, this time it was passed through the pre-column containing $\text{Eu}(\text{fod})_3$ -Porasil maintained at 100°C . The compounds not complexed were thermally focused and analyzed. Those compounds that were eluted through the pre-column included chloroform, cyclohexane and toluene, as expected. The pre-column was then heated to 150°C while backflushing with carrier gas into the gas chromatograph. The analysis showed that both ethyl acetate and methyl isopropyl ketone had been complexed and subsequently desorbed upon heating the $\text{Eu}(\text{fod})_3$ pre-column.

The above examples demonstrate the effectiveness of the lanthanide chelate in selectively retaining certain compounds in a number of applications. The last example, the sorption-desorption of species, is indeed the ideal for this system. The major problem experienced in the preliminary studies occurred in the attempts to desorb samples from $\text{Eu}(\text{fod})_3$. $\text{Eu}(\text{fod})_3$ is itself appreciably volatile and a large amount of "bleed" from the $\text{Eu}(\text{fod})_3$ -Porasil column was obtained when it was heated above 100°C . In the previous examples the $\text{Eu}(\text{fod})_3$ was not analyzed in the chromatogram because it simply will not elute from the Carbowack column at the temperatures employed for very volatile compounds. It is for this reason that the much less volatile fluorinated β -diketonate complex was synthesized.

Eu-dihed chelate interactions with nucleophiles

As a test of the range over which the new lanthanide chelate column is effective a homologous series of hydrocarbons and a series of methyl esters were dissolved in methanol and directly injected into a Tenax trap. The methanol was removed by passing dry carrier gas through the Tenax trap. The compounds on Tenax were then thermally desorbed and passed into the lanthanide column which was maintained at 125°C. Compounds that were eluted through the lanthanide column within 4 min were thermally focused on the cooled analytical column followed by analysis.

Fig. 3 shows that the compounds that were eluted through the lanthanide column at 125°C were *n*-heptane, *n*-nonane, *n*-undecane, *n*-dodecane and most of the tridecane. No esters were eluted through the pre-column even though methyl acetate, methyl propionate, methyl butyrate, methyl hexanoate, and methyl octanoate are all more volatile than *n*-tridecane. The esters were retained selectively, presumably due to thermally reversible complex formation with [Eu(dihed)]_x. This is expected based upon independent NMR shift reagent studies in which Eu(fod)₃ was employed. The second analysis, that of the retained compounds, shows all of the esters in addition to the higher-molecular-weight hydrocarbons starting with the portion of *n*-tridecane not fully eluted in the first chromatogram. Thus one might say that the selectivity of [Eu(dihed)]_x at 125°C is effective over the range of E₂ (methyl acetate) to C₁₃ (tridecane). The higher-molecular-weight hydrocarbons are not complexed but are retained due simply to non-specific solubilization in the SE-30-lanthanide chelate liquid phase.

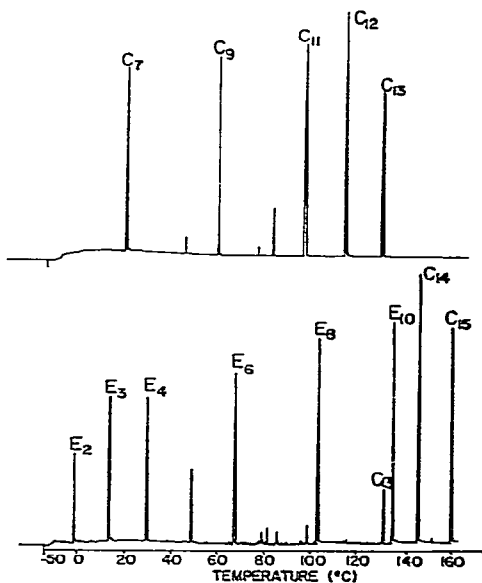


Fig. 3. The separation of a mixture of normal hydrocarbons and methyl esters on [Eu(dihed)]_x. The top chromatogram shows the elution of those compounds that are not retained by the [Eu(dihed)]_x pre-column at 125°C. The bottom chromatogram results when the compounds retained at 125°C are thermally desorbed for 4 min at 225°C and analyzed separately. In this example E₂ = methyl acetate, C₇ = *n*-heptane. Analytical column conditions: 30-m SE-52 fused silica capillary column, He at 17 p.s.i., split 30 ml/min temperature program: thermal focusing at -50°C then from 0 to 200°C at 4°/min.

If one maintains the lanthanide column at 175°C during complexation a different separation is obtained. The lanthanide column is then too hot to retain the most volatile esters, as is shown in the top trace of Fig. 4. The less volatile esters are still retained, but methyl acetate, methyl propionate and methyl butyrate are lost. However, fewer hydrocarbons are retained in the pre-column. Tridecane, tetradecane and pentadecane are not retained at 175°C. Thus the useful analytical range at 175°C is E₄ (methyl butyrate) to C₁₆ (hexadecane). The selectivity has not necessarily been extended but rather covers a different range of volatilities of analytes.

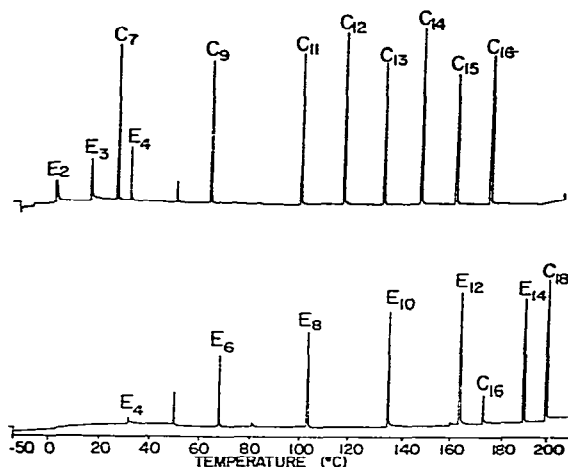


Fig. 4. The separation of the mixture in Fig. 3 performed while the [Eu(dihed)]_x pre-column is maintained at 175°C, showing a change in the volatility range of analytes for which the sorbent is effective. Same analytical conditions as Fig. 3, except the temperature during sorption of [Eu(dihed)]_x pre-column.

Applications of selective lanthanide sorbents

The ability to shift the effective retentive complexation of the lanthanide sorbent through the use of temperature changes has important practical applications. This is illustrated in the analysis of very complex mixtures. The top trace in Fig. 5 shows the chromatogram resulting when 0.1 μ l of a cologne essence is injected directly onto Tenax, then thermally desorbed and analyzed as a total mixture. If one analyzes a second aliquot by first passing the mixture through the [Eu(dihed)]_x sorbent maintained at a temperature of 175°C, the middle trace results, in which approximately one-half of the compounds have been removed. Desorption of the lanthanide column at 225°C and subsequent analysis of the compounds removed from the [Eu(dihed)]_x sorbent resulted in the bottom chromatogram in Fig. 5. Several features of the chromatograms are noteworthy. The example shows most of the non-retained compounds being eluted early in the chromatogram. Whereas only myrcene has so far been positively identified by GC-MS, the mass spectra of other compounds indicate that they are similar compounds, *i.e.*, saturated or unsaturated hydrocarbons. Later in the chromatogram geranyl acetate and acetylnaphthalene were identified and these were retained by the europium sorbent as was expected. Thus the separation of the sample into complexed and non-complexed fractions was achieved.

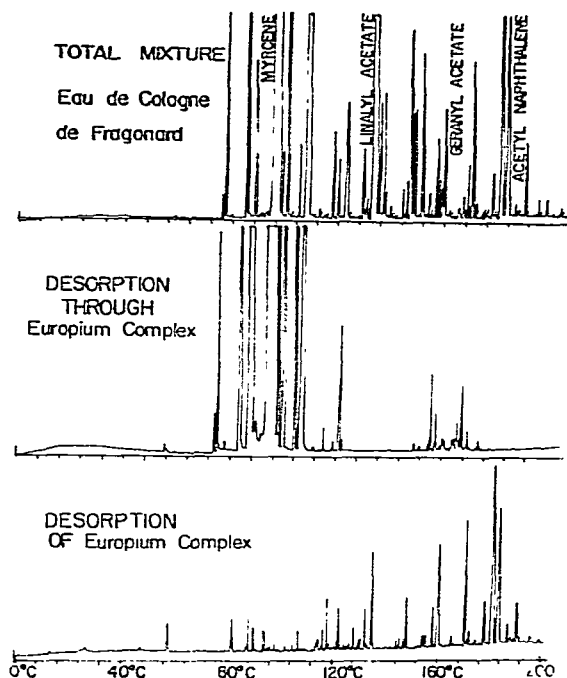
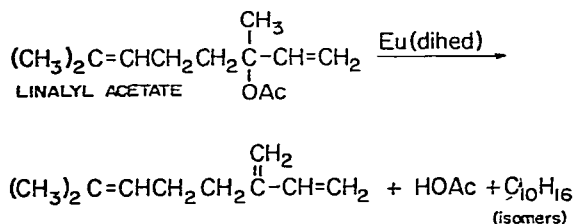


Fig. 5. Separation of the volatile compounds in a cologne essence. The top chromatogram shows the analysis of the total mixture. The middle chromatogram is the analysis of the non-retained compounds. The bottom chromatogram is the analysis of the retained compounds. The $[\text{Eu}(\text{dihed})]_2$ column was maintained at 175°C during sorption and was heated to 225°C to recover the retained compounds. Analytical conditions: same as in Fig. 3.

One negative aspect of the selective sorbent, however, resulted in the case of linalyl acetate. This compound, which is present in the total mixture, is absent in both the complexed and uncomplexed fractions. This was determined to result from the loss of acetic acid from linalyl acetate which produces several $\text{C}_{10}\text{H}_{16}$ isomers, of which the major constituent is shown in the reaction below:



Although it is unfortunate that the sorbent catalyzes the decomposition of linalyl acetate, it is not unexpected in this case. Linalol, the alcohol from which linalyl acetate is derived has been previously described as thermally labile in gas chromatographic systems²⁰. Thus it is not surprising that in contact with a strong Lewis acid

such as the lanthanide sorbent, the normally stable acetate can undergo such a reaction. This behavior is not expected to be exhibited by the large majority of oxygen and nitrogen containing compounds.

Tobacco smoke analysis

One of the most challenging trace analysis problems is the separation of mixtures resulting from pyrolysis. A large amount of research has been done on the constituents of tobacco smoke both in the area of volatile compounds as well as fractions arising from wet chemical separations of smoke condensates. It is our purpose here not to add to the already enormous list of compounds identified in cigarette smoke, but rather to present a method which may have applicability for detailed studies in this or similar areas.

The top trace in Fig. 6 shows the chromatogram resulting when an approximately 1-ml "puff" of cigarette smoke is sorbed on Tenax and then the volatile organics are desorbed into the cooled fused silica capillary column, followed by temperature programmed analysis. Even the superb resolution available from the fused silica capillary column is not sufficiently high to resolve many of the compounds, especially those present at lower levels.

Through the use of the lanthanide sorbent most of the oxygenated compounds in the mixture can be removed from the very complex mixture and analyzed in a separate fraction. These include a series of methyl ketones and aldehydes. The non-

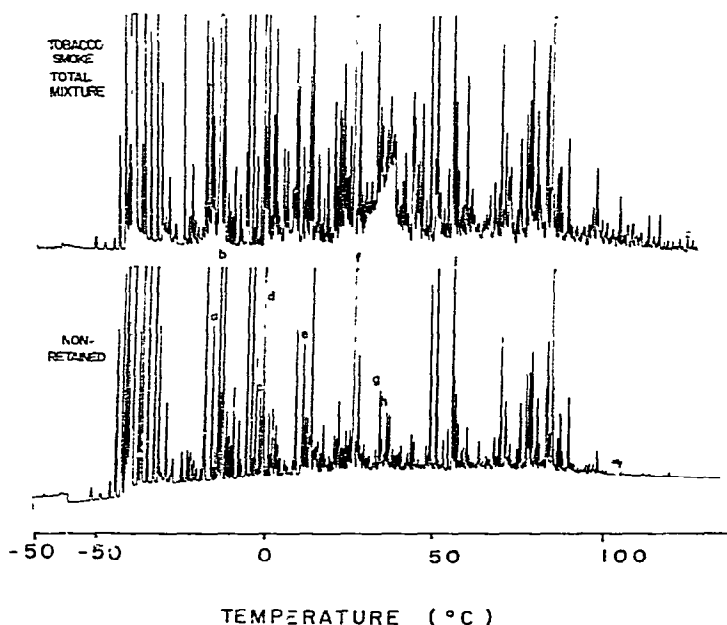


Fig. 6. Chromatograms of the volatile compounds in tobacco smoke. The top trace is the total mixture. The bottom trace shows the analysis of the non-retained compounds. a = *n*-Hexane, b = 2-methylfuran, c = *n*-heptane, d = benzene, e = *n*-octane, f = 2,5-dimethylfuran, g = toluene, h = *n*-nonane, i = *o*-xylene. Analytical column conditions: 30-m SE-52 fused silica capillary column, He at 15.5 p.s.i., split 60 ml/min, thermal focused at -50°C for 4 min then at $2^{\circ}/\text{min}$ to 100°C .

retained fraction is also made more tractable with regards to identification and quantitation.

The effect of the temperature at which the compounds are sorbed is again quite crucial. In the case of the cologne essence the sorption took place at relatively high temperature since the compounds were less volatile. In the present example a lower volatility fraction was separated; consequently the sorbent was maintained at only 75°C. The analysis of compounds not retained by the lanthanide sorbent at this temperature is shown in the bottom trace of Fig. 6. Identification of some of the major peaks was accomplished using mass spectral data and retention times of standard compounds. Desorption of the [Eu(dihed)]_x column at 180°C resulted in the bottom trace in Fig. 7 shown with the total mixture for comparison. Compound identification was again made using mass spectral and retention time data.

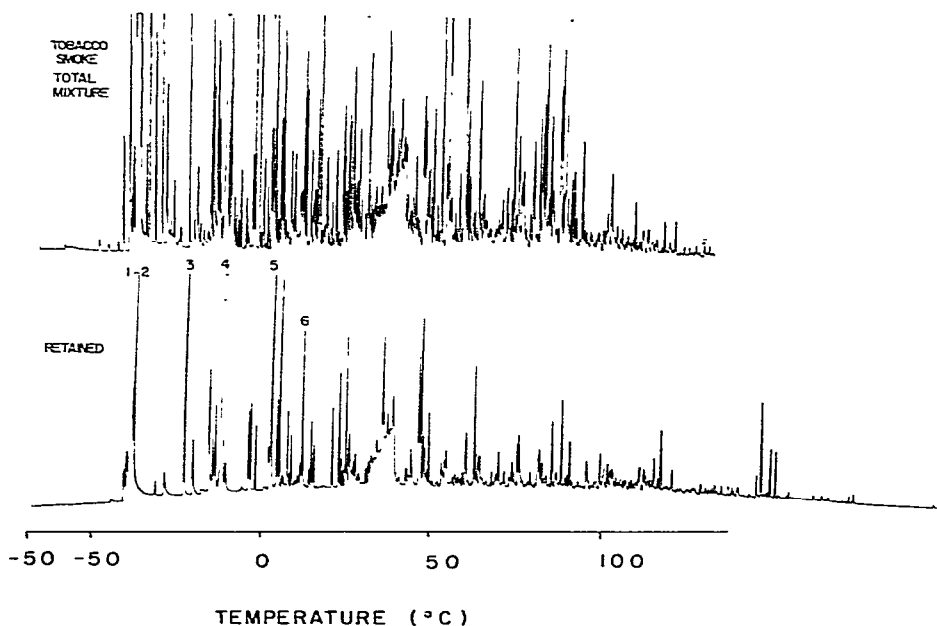


Fig. 7. Chromatogram of the compounds in tobacco smoke that are complexed and retained by the [Eu(dihed)]_x pre-column (below) shown with the total mixture (above). 1 = Propanone, 2 = propanal, 3 = 2-methylpropanal, 4 = butanone, 5 = 3-methylbutanal, 6 = 2-pentanone. Same analytical conditions as in Fig. 6.

Two of the compounds identified in the fractions appear to behave in an anomalous manner. Both 2-methylfuran and 2,5-dimethylfuran are not retained by the pre-column even though these compounds contain oxygen. NMR studies using paramagnetic lanthanide shift reagents have shown that neither 2-methylfuran nor furan show induced chemical shifts with lanthanide chelates. Tetrahydrofuran in the presence of Eu(fod)₃ exhibits very marked NMR shifts and is retained by lanthanide-containing sorbents. The furans, by contrast, are not good donors and thus are not retained by the pre-columns.

In the work described above, we have utilized only europium as the metal

in the chelate. In experiments using the smaller lanthanide, lutetium, we have seen results almost identical to the work with europium. One can assume that any of the lanthanides will behave in a like manner. This would allow the use of less expensive, more common, lanthanide metals (e.g., lanthanum) to be used for this purpose. The use of lanthanide containing pre-columns, thus, shows great flexibility and promise for achieving class separations prior to gas chromatographic analysis of highly complex mixtures.

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