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## APPLICATIONS OF SELECTIVE COMPLEXATION BY A EUROPIUM(III) COORDINATION POLYMER SORBENT FOR THE PRE-FRACTIONATION OF VOLATILE COMPOUNDS

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### SUMMARY

Non-volatile coordination polymers of the lanthanides can be formed from the reaction of the metal salt with a bis( $\beta$ -diketonate) ligand. The resulting polymer is incorporated into the stationary phase of a small, pre-analytical column and used selectively to retain nucleophilic organic compounds through complexation. Compounds which do not form complexes, or form weak complexes, are eluted through the pre-column and analyzed by high resolution capillary gas chromatography. The retained compounds are subsequently removed from the pre-column by heating, which dissociates the complex. Carrier gas sweeps the pre-column and the previously sorbed compounds are deposited in the analytical column for analysis as a separate fraction. The technique is applied here to the separation of complex forming and non-complex forming components arising from volatile urinary metabolites and gasoline decomposition products.

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### INTRODUCTION

In a recent paper we described the synthesis of a novel bis( $\beta$ -diketone), H<sub>2</sub>dihed, [*p*-di(4,4,5,5,6,6,6-heptafluoro-1,3-hexanedionyl)benzene] which has the ability to form coordination polymers with the lanthanides<sup>1</sup>. The polymers retain the excellent Lewis acidity characteristic of previously synthesized fluorinated tris( $\beta$ -diketonates)<sup>2,3</sup>, yet are extremely non-volatile and hence more suitable for use as stationary phases in gas chromatography (GC). When incorporated into a pre-analytical column, the polymers were shown to be effective in separating oxygenated compounds from hydrocarbons and chlorinated hydrocarbons, based upon complexation between the nucleophilic oxygen and the coordinatively unsaturated lanthanide.

The pre-column sorbent was applied to the separation of complex-forming from non-complex-forming solutes in the analysis of volatile organic compounds in wastewater effluent, a fragrance essence and tobacco smoke. In each case a separation into two fractions was accomplished, producing simplified chromatograms. The net result was facilitated identification of compounds by mass spectral and retention time matching techniques.

We report here two additional applications of this selective sorbent as well as introduce new data concerning the characterization of the lanthanide polymer previously described.

## EXPERIMENTAL

### *Gas switching assembly and chromatograph*

A dual-sorbent gas switching assembly has been described previously<sup>1</sup>; a schematic of the selective sorption and desorption flow systems is shown in Fig. 1. Multiport valves permit three different modes of operation: (a) total mixture analysis, (b) non-complexed fraction analysis and (c) thermal desorption and analysis of the complexed fraction. In (a) compounds trapped on a porous polymer [(Tenax GC, poly-(2,6-diphenyl-*p*-phenylene oxide)] can be thermally desorbed directly into the cooled analytical column. This results in a chromatogram containing all the desorbed compounds, which is referred to as the total mixture.

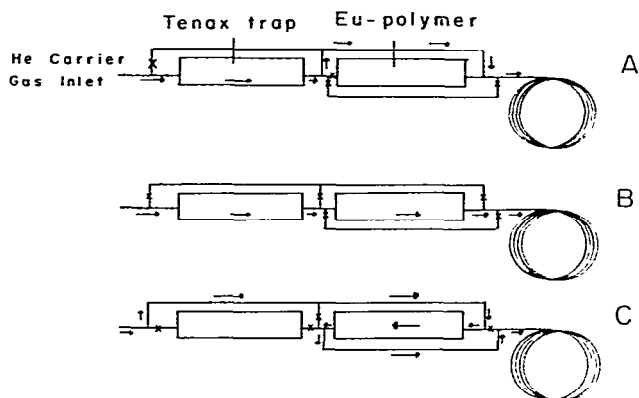


Fig. 1. Schematic of gas flow in three modes of analysis.  $\times$  represents blocked flow. A, Total mixture analysis, by-passing the Eu-polymer sorbent. The sample is first sorbed on a Tenax column, then thermally desorbed at 200°C into a cooled fused silica capillary column, followed by temperature programming the analytical column. B, Analysis of the fraction of the sample not retained by the Eu-polymer sorbent. C, Thermal desorption of complexed compounds at 220°C, followed by capillary chromatography.

Alternatively, in (b) compounds exiting from the Tenax trap can be directed into the selective sorbent column. Those compounds that are eluted through the selective sorbent flow into the cooled ( $-50^{\circ}\text{C}$ ) analytical column for thermal focusing. Following temperature programming, a chromatogram of the non-complex forming solutes is obtained.

In the third mode of analysis, (c), the valves are rotated so that pure carrier gas backflushes the selective sorbent pre-column. The pre-column is heated and the previously complexed compounds are eluted into the analytical column and analyzed as described<sup>1</sup>. In (c), the chromatogram obtained contains the complex-forming compounds and is referred to here as the retained fraction.

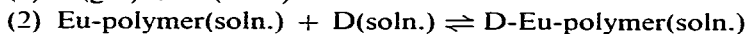
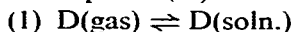
The sorbent system was mounted on a Hewlett-Packard Model 5830 gas chromatograph equipped with a Grob-type capillary injection port and a flame-ionization detector. The exit line from the sorbent system was connected to the carrier gas inlet

of the injection port. A 30 m  $\times$  0.31 mm I.D. SE-54 fused silica capillary column (J & W Scientific, Orangevale, CA, U.S.A.) was installed in the chromatograph.

## RESULTS AND DISCUSSION

Many environmental and biological samples contain so many compounds that they are not completely separated even with the highest resolution fused silica capillary columns one can prepare or obtain. Peaks frequently overlap and the mass spectra of two or more co-eluting compounds are so complex that it is difficult or frequently impossible to identify the unknown compounds giving rise to the spectra. In the face of such complexity it becomes necessary to consider techniques for compound class separations that can be accomplished prior to introduction into the capillary column. For this purpose many techniques can be employed, but one of the simplest, yet effective methods is based upon reversible metal complex formation. If a polymer containing a suitable metal ion is used as a selective sorbent, compound class pre-separation can be effected before the fractions are thermally focussed for subsequent separation in the analytical capillary column. Extensive studies of lanthanide chelates as nuclear magnetic resonance (NMR) shift reagents have provided ample evidence that reversible complexes can be formed.

Fluorinated  $\beta$ -diketonate chelates of the lanthanides can function as Lewis acids in reactions with organic compounds. Since the coordinatively unsaturated metal is able to accept additional donor atoms in the coordination sphere, compounds having moieties capable of donating electrons can form relatively strong complexes with these chelates. If a metal such as europium(III) (Eu) is incorporated into a coordination polymer, then dissolved in a polydimethylsiloxane stationary phase of a small gas chromatographic pre-column, the following equilibria occur when nucleophiles (D) are introduced:



At relatively low temperatures (*e.g.*, 25°C) the equilibrium for many donor compounds lies far to the right in both equations. Heating of the Eu polymeric sorbent, however, affects not only the complexation equilibrium but also the partitioning of compounds between the gas and liquid phases. The result is that, upon heating, compounds are removed from the liquid phase and the pre-column by carrier gas flow.

Consequently, one can achieve class separations of complexing compounds from those that do not form stable complexes (or are highly volatile) in a short pre-column before transferring the fractions to the high resolution capillary column. Examples of compound classes that form complexes with Eu and are retained include ketones, aldehydes, alcohols and carboxylic acids. By contrast, aliphatic, olefinic, aromatic and chlorinated hydrocarbons are not retained (unless they have much lower volatilities than the complex-forming compounds). Examples of the application of selective sorbent class separations have been demonstrated in the analysis of volatiles in urine and in the identification of minor constituents formed by oxidative degradation of gasoline.

We have shown that selective complexation allows one to separate a hopelessly complex mixture into two somewhat more manageable fractions—one containing re-

tained nucleophilic compounds, the other, the non-retained. With simpler chromatograms containing fewer overlapping peaks, it becomes much easier to make identifications of unknown compounds and quantitation can be effected more readily. Furthermore, the mass spectra are easier to interpret when fewer compounds are eluted as each spectrum is scanned.

*Characterization of the Eu-dihed complex and the ligand from which it is synthesized*

Elemental analyses were performed on five synthesized batches of the Eu complex and the free ligand, H<sub>2</sub>dihed. Representative results are shown in Table I. The data for the different syntheses of the Eu-dihed complex indicated that the percent carbon varies from roughly 26% to about 33% carbon. There is intrinsic imprecision in the analysis for fluorine even when the C, H data are accurate, as in the case of the uncomplexed ligands. Since the polymeric complexes are capable of forming adducts with donor molecules such as water, and the percentage of hydrogen is low, an empirical formula for the complex was determined from the carbon to metal ratio without regard to hydrogen content. In the case shown, designated [NaEu<sub>2</sub>(dihed)<sub>3</sub>-NO<sub>3</sub>]<sub>x</sub>, the empirical formula based on this ratio was determined to be closest to three dihed units to two Eu ions.

TABLE I

ELEMENTAL ANALYSES OF H<sub>2</sub>dihed AND [NaEu<sub>2</sub>(dihed)<sub>3</sub>NO<sub>3</sub>]<sub>x</sub> COMPLEXES

Analysis after drying to constant weight.

|  | <i>Found</i>  |      |       |      |       |      |
|--|---------------|------|-------|------|-------|------|
|  | <i>Calc'd</i> |      |       |      |       |      |
|  | %C            | %H   | %F    | %N   | %Eu   | %Na  |
| H <sub>2</sub> dihed   | 38.91         | 1.47 | 49.41 |      |       |      |
|  | 39.01         | 1.45 | 47.99 |      |       |      |
| [NaEu <sub>2</sub> (dihed) <sub>3</sub> NO <sub>3</sub> ] <sub>x</sub> | 32.28         | 0.97 | 42.92 | 0.82 | 14.7* | 0.9  |
|  | 31.71         | 0.88 | 39.01 | 0.68 | 14.86 | 1.12 |

\* Eu analysis by direct ignition; an analysis by digestion, followed by oxalate formation, then ignition to oxide resulted in a Eu value of 16.0%.

This ratio and the structure shown in Fig. 2 are only approximate; chain cross-linking is also possible. Since the ligand is a bis(bidentate) complexing agent and the metal can accept 1, 2, 3, or possibly 4 bidentate groups, many non-stoichiometric combinations of metal and ligand are possible. The presence of a small amount of sodium is due to the method of preparation (*i.e.*, neutralization of ligand by 4 M NaOH) and represents approximately one sodium ion per empirical formula in the present example. Nitrogen probably is present as the nitrate ion which is the counterion of Eu(III) in one starting material and may be carried by the product to maintain electrical neutrality in the polymeric complex, either weakly bonded to Eu(III) or as a counter-ion. The [Eu<sub>2</sub>(dihed)<sub>3</sub>]<sub>x</sub> complex contains an average of one nitrate ion for every two Eu centers: Therefore a more complete empirical formula would be [NaEu<sub>2</sub>(dihed)<sub>3</sub>NO<sub>3</sub>]<sub>x</sub>. Many other structures, some involving cross-linking of the polymer,

can be envisioned. Because there are so many possible structures, the general symbol,  $[\text{Eu}(\text{dihed})]_x$  will represent these throughout this paper, but the closest actual stoichiometry appears to be  $[\text{NaEu}_2(\text{dihed})_3\text{NO}_3]_x$ .

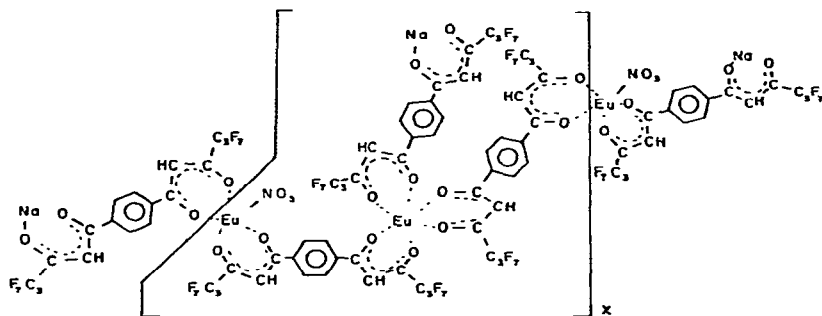


Fig. 2. Proposed generalized structure of the polymer  $[\text{NaEu}_2(\text{dihed})_3\text{NO}_3]_x$ . Additional donor sites on the metal may be occupied by water, cross-linking keto moieties in dihed, and/or solvent molecules.

Mass spectra and proton NMR spectra of the free ligand were measured. The mass spectrum of the free ligand displays a molecular ion at 554 atomic mass units (a.m.u.) of intensity 23 relative to the base peak at 385 a.m.u. (intensity = 100). The peak results from loss of the fragment  $\text{C}_3\text{F}_7^+$  from the parent peak. A peak at 343 a.m.u. (intensity = 10) results from loss of  $\text{C}_3\text{F}_7\text{COCH}_2^+$  from the parent or loss of  $\text{COCH}_2$  from the base fragment. Other major peaks include 69 a.m.u. ( $\text{CF}_3^+$ ) and 239 a.m.u. ( $\text{F}_7\text{C}_3\text{COCH}_2\text{CO}^+$ ).

The proton magnetic resonance spectrum of  $\text{H}_2\text{dihed}$  in  $\text{CDCl}_3$  solution shows a small singlet (relative area = 1) at  $\delta = 2.67$ , attributed as likely arising from the  $-\text{CH}_2-$  protons in the keto form. The two resonances at  $\delta = 6.70$  (rel. area 32.5) and at  $\delta = 8.13$  (relative area = 59) result from the methine proton or enol form of the molecule and aromatic protons, respectively. No peak resulting from the OH of the  $\beta$ -diketone in the enol form (which, if visible, is usually seen in the range 12–16  $\delta$ ) was seen, most likely due to severe broadening. From these data it can be concluded that the ligand is present as greater than 98% enol form in  $\text{CDCl}_3$  solution.

Since the free ligand is a multidentate bis( $\beta$ -diketone), complexes of it with the lanthanides have the ability to form high molecular weight coordination polymers. Two methods of estimating the approximate molecular weight were used: vapor pressure osmometry (VPO) and gel permeation chromatography. The VPO measurements on a sample of the europium polymer, performed by Huffman Laboratories, indicated a molecular weight of 4330 at a concentration of 15.33 mg/ml in methanol at 45°C. Since the sample was only sparingly soluble in methanol, a very low response in the vapor pressure osmometer was produced.

Independent confirmation of the approximate molecular weight was obtained by gel permeation chromatography studies. These indicated that the molecular weight in dimethylformamide is greater than 4000. Since both methanol and dimethylformamide are complexing solvents, the molecular weight of the Eu polymer dissolved in SE-30 silicone gum may actually be substantially higher. Samples of the solid polymer were subjected to thermo-gravimetric analysis. With a flowing helium atmosphere there was no significant weight loss at temperatures below 290°C. There

is a slight darkening of the bright yellow polymer at temperatures above 270°C, however. The sorbent was prepared as described earlier<sup>1</sup>.

*Class separation of complexing vs. non-complexing volatile constituents of urine*

The possibility of early diagnosis of disease-states through the examination of the complex mixtures in biological fluids is a very active area of investigation. Sophisticated separation and identification procedures for organic compounds, coupled with statistical analyses, may some day make possible the prediction of many diseases well before symptoms of that disease develop overtly. In the case of *diabetes mellitus*, volatile metabolites in the urine may signal early stages of disease development. A

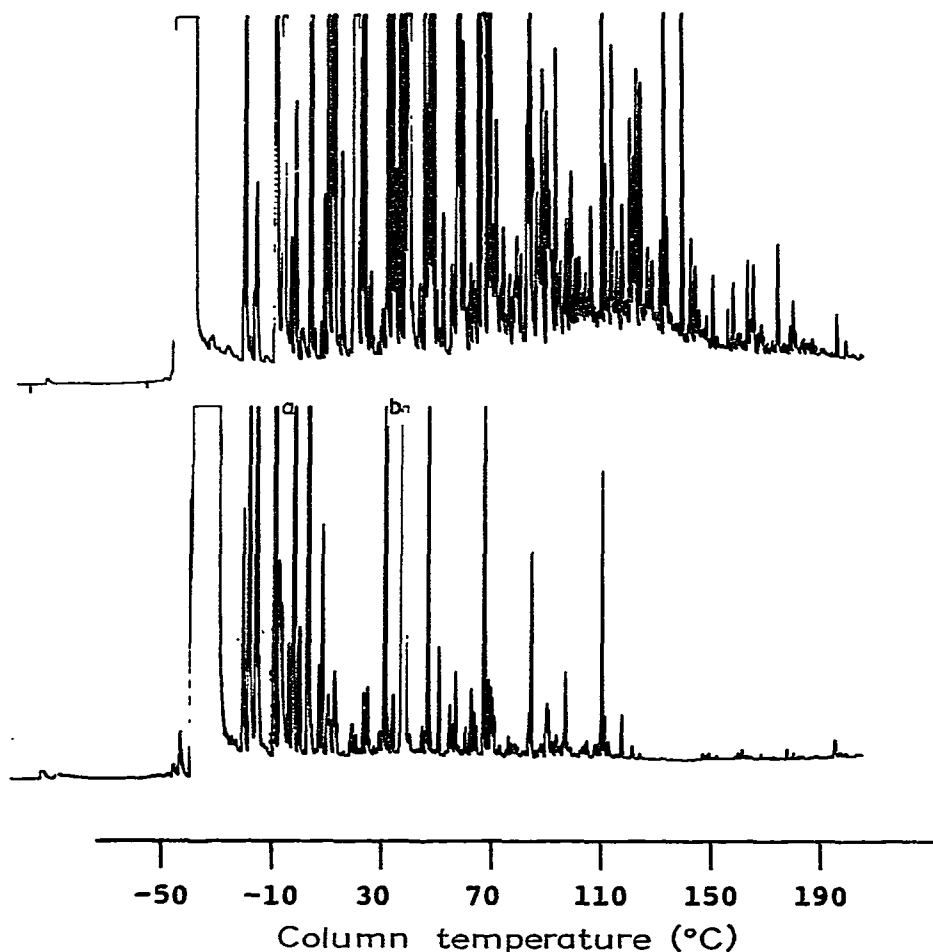


Fig. 3. Chromatograms of the total mixture (top) and the non-retained fractions (bottom) of volatile constituents of urine. Analytical conditions: Hewlett-Packard Model 5830A gas chromatograph equipped with a 30 m  $\times$  0.31 mm I.D. SE-54 fused silica capillary column. He at 11 p.s.i.g., split 30 ml/min, thermal focusing at  $-50^{\circ}\text{C}$  for 9 min, then  $-50$  to  $200^{\circ}\text{C}$  at  $4^{\circ}\text{C}/\text{min}$ . Identifications: a = chloroform, b = toluene. The pre-column was maintained at  $100^{\circ}\text{C}$  during the collection of the complexed fraction and the elution of the non-complexed fraction into the cooled capillary column. The flow through the sorbent system was reduced, relative to conditions used previously<sup>1</sup>, to 5 ml/min by reducing the split flow.

number of investigators have obtained profiles of the volatile metabolites in the urine of normal and diseased individuals, and a substantial number of compounds have been catalogued as existing in high concentrations only in the diseased subjects<sup>4-6</sup>. These compounds, almost all of which contain a complex-forming oxygen functionality such as a keto or hydroxyl group, can be removed selectively from the metabolite mixture by the europium sorbent, resulting in a more specific and simplified analysis of indicator compounds.

A sampling system similar to the one described by Zlatkis *et al.*<sup>4</sup> for headspace analysis was constructed. A 100-ml sample of urine was heated to approximately 67°C in a 3-necked flask with stirring. Helium purge gas was passed over the surface of the urine, up through a water cooled condenser and into a Tenax trap at a rate of 30 ml/min for 1 h. The Tenax trap was then removed and thermally desorbed under flowing helium into the cooled capillary analytical column. Fig. 3 shows the chromatograms obtained from the total mixture and subsequently from the unretained fraction of another aliquot of the same sample passed through the Eu polymer.

The top chromatogram in Fig. 4 shows the separation of the total mixture again to facilitate comparison, along with the bottom chromatogram of the retained fraction obtained following thermal desorption of the Eu polymer at 220°C. In these fractionations the Eu trap was maintained at 100°C during the selective sorption step. Since some of the volatile components of normal urine are expected to be ketones, standards of ketones in methanol were analyzed in order to match retention times. The retention times of major peaks in both the retained fraction and the total mixture matched the retention times of the ketone standards (acetone, butanone, 2-pentanone, 4-heptanone), all of which have been shown to be major urinary metabolites. Two large peaks in the non-retained fraction were identified by retention times as chloroform and toluene, again known to be present at relatively high concentrations in urine.

Further identification and quantitation might be possible if deemed desirable but the purpose of this experiment was to demonstrate that complex-forming compounds can be separated from non-complexing by the selective Eu sorbent. In the case of diabetics, the absence or presence of large amounts of branched and normal alcohols seems to be a particularly good indicator of disease<sup>4</sup>. Alcohols have been shown to be retained by this pre-column and would appear in the retained fraction, if present. Thus the use of this pre-column for class separation of complex-forming ketones and alcohols should be simpler and more definitive for identification of disease states than procedures heretofore employed.

#### *Selective sorption of decomposition products in gasoline*

The separation of complex mixtures into an "oxygenated" fraction and a "hydrocarbon" fraction demonstrates very nicely the ability of the Eu sorbent to simplify chromatograms and provide some insight into the functional class of a particular compound.

One powerful attribute of the selective lanthanide sorbent lies in the ability to "recognize" the functional class of a particular compound. The sorbent can remove even trace constituents from a non-complexing matrix if they can form complexes with a lanthanide ion such as Eu. An excellent example of this ability is seen in the analysis of trace level decomposition products in gasoline.

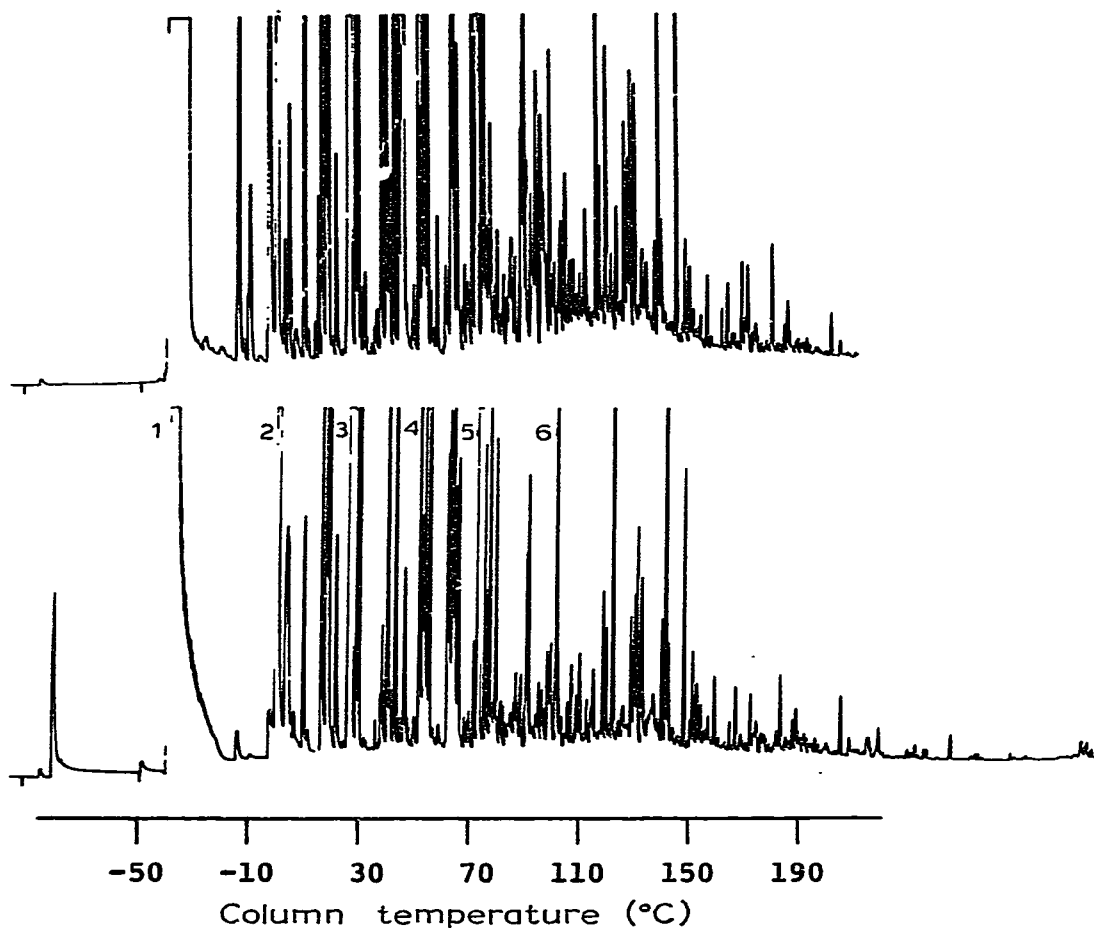


Fig. 4. Chromatograms showing the total mixture (top) and the retained fraction (bottom) obtained from volatile urinary constituents that form complexes with the Eu polymer, and are subsequently dissociated by thermal desorption into the cooled analytical capillary column. The analytical conditions were identical to those in Fig. 3. Peaks: 1 = acetone, 2 = butanone, 3 = 2-pentanone, 4 = 3-methyl-2-pentanone, 5 = 4-heptanone, 6 = 2-octanone.

It has been known for quite some time that certain constituents in gasoline and other hydrocarbon fuels slowly decompose when exposed to the oxygen in air<sup>7</sup>. Particularly susceptible are gasolines with high olefin contents, since olefins more easily react with oxygen than do aromatic or aliphatic hydrocarbons. Oxidation of selected olefins by molecular oxygen has been extensively studied; the products of attack of olefins by oxygen have been shown to include aldehydes, ketones, hydroperoxides, epoxides, alcohols, acids and esters<sup>8-10</sup>. Those in the petroleum industry are particularly concerned about the stability of a product exposed to air. Tests are routinely performed to determine the ease with which a fuel sample can be degraded. One such test consists of subjecting a sample of fuel to oxygen under pressure at elevated temperatures. The pressure is monitored over some period, and a drop in pressure is indicative of oxygen consumption by the fuel. The length of time required and the



degree of pressure drop are indications of the stability of the fuel sample<sup>11</sup> and its resistance to form gums and more volatile oxygenates.

A 50-ml volume of polymer-cracked gasoline, represented by the supplier (Asamera Oil, Denver, CO, U.S.A.) to be virtually 100% olefins, was subjected to an oxygen pressure of 5.8 atm at 100°C. Over the course of about 5 h virtually all the oxygen was consumed. The volume of the bomb was estimated to be 400 cm<sup>3</sup>, which would be equivalent to a consumption of 2.1 g (0.066 mole) of oxygen.

The NMR spectra of both the non-degraded gasoline and the degraded material was obtained. An interesting feature of the two spectra is the small percentage (less than 5%) of vinyl protons. If one assumes the gasoline to be 100% olefins with an average molecular weight of about 114 a.m.u., the gasoline must consist of a very high percentage of tri- and tetra-substituted olefins. Oxidation of these species would be expected to yield a higher percentage of ketones, rather than aldehydes<sup>7</sup>. This was subsequently confirmed in the gas chromatographic analysis.

Oxygen-degraded and undegraded gasoline were subjected to analysis following the Eu sorbent pre-separation using the system described earlier<sup>1</sup> and in Fig. 1. Sampling was accomplished by diluting the gasoline in methanol and directly injecting a liquid aliquot of the solution into the Tenax trap. The methanol was removed by passing carrier gas through the trap (at ambient temperature) in the reverse direction at a flow-rate of 20 ml/min. The Tenax trap was then positioned in the valve system and analyzed by thermal desorption as usual.

Fig. 5 (top) contains the results obtained from GC analysis of the non-retained fraction of the undegraded gasoline. The few large peaks in the retained fraction

TABLE II

TRACE CONSTITUENTS IDENTIFIED IN DEGRADED GASOLINE COMPLEXED FRACTION

| Peak number | Compound  | Identified by     |       | Molecular weight from CI-MS |
|-------------|---|-------------------|-------|-----------------------------|
|             |   | GC retention time | EI-MS |                             |
| 1           | Acetone   | ×                 | ×     |                             |
| 2           | <i>n</i> -Propanal  |                   | ×     |                             |
| 3           | 2-Methylpropanal  | ×                 | ×     |                             |
| 4           | <i>n</i> -Butanal   | ×                 | ×     |                             |
| 5           | Butanone  | ×                 | ×     |                             |
| 6           | 3-Methyl-2-butanone   | ×                 | ×     |                             |
| 7           | 3-Methylbutanal   | ×                 | ×     |                             |
| 8           | 3-Methylbuten-2-one   |                   | ×     |                             |
|             | Acetic acid   |                   | ×     |                             |
| 9           | 2-Pentanone   | ×                 | ×     |                             |
| 10          | 3-Methyl-2-pentanone  | ×                 | ×     | 100                         |
| 11          | C <sub>7</sub> H <sub>12</sub> O Isomer                       |                   | ×     | 112                         |
| 12          | [(CH <sub>3</sub> ) <sub>2</sub> SiO] <sub>3</sub> (artifact) |                   | ×     | 222                         |
|             | Butanoic acid   |                   | ×     |                             |
| 13          | Heptanal  | ×                 | ×     | 114                         |
| 14          | Octanal   | ×                 | ×     | 128                         |
| 15          | Nonanal   | ×                 | ×     | 142                         |
| 16          | Decanal   | ×                 | ×     | 156                         |

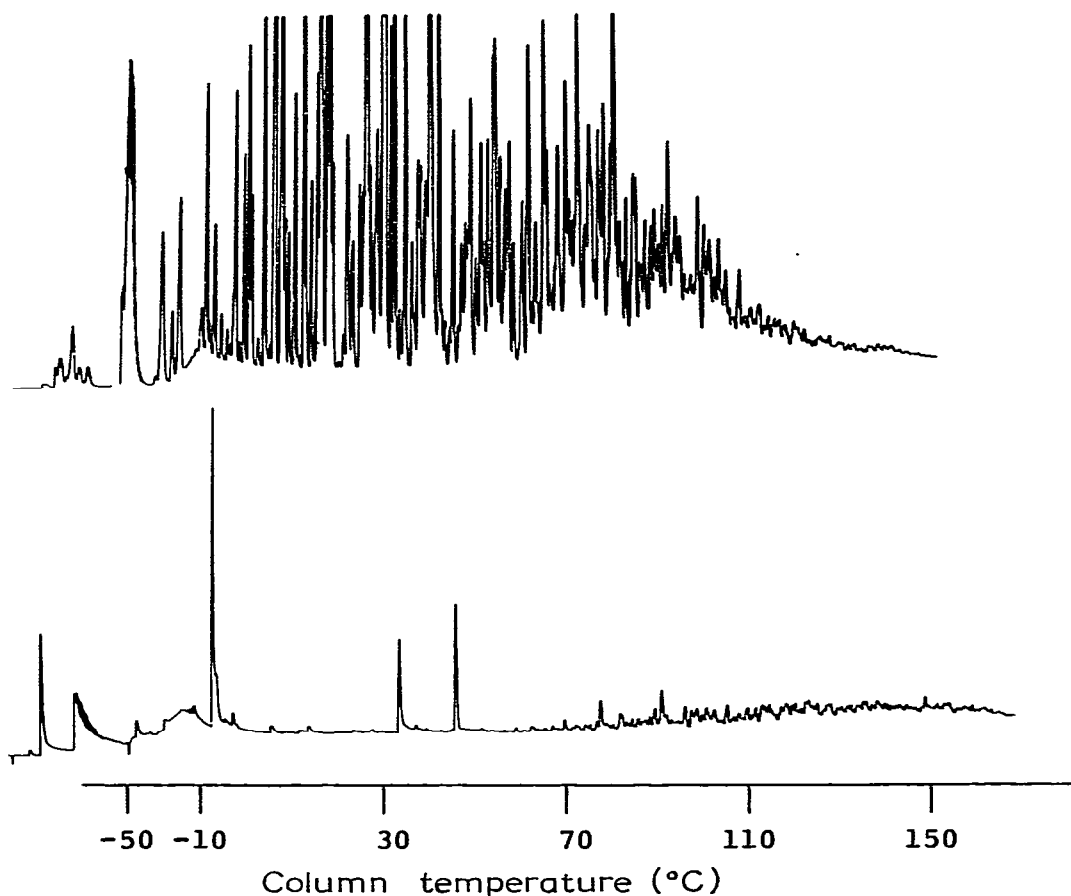


Fig. 5. Chromatograms showing the non-retained (top) and the retained fractions (bottom) obtained from the separation of the gasoline sample before oxidative degradation. Analytical conditions: 30 m  $\times$  0.31 mm I.D. SE-54 fused silica capillary column, He at 11 p.s.i.g., split 5 ml/min, fractions thermally focused at  $-50^{\circ}\text{C}$ , then  $-50$  to  $-10^{\circ}\text{C}$  at  $10^{\circ}\text{C}/\text{min}$ , then  $-10$  to  $180^{\circ}\text{C}$  at  $2^{\circ}\text{C}/\text{min}$ .

(bottom) result from artifacts being removed from the Eu sorbent column during thermal desorption. One of the artifacts results from the siloxane polymer and is listed in Table II. The other contains the  $\text{C}_3\text{F}_7$ -functional group and is presumed to result from slight decomposition of the dihed polymer. Only trace levels of compounds present in undegraded gasoline appear in the retained fraction. After degradation of the gasoline by oxygen the chromatograms in Fig. 6 were obtained. The chromatogram of the non-retained fraction appears almost identical (perhaps a slightly smaller sample size), but the retained fraction shows that numerous complexing compounds have been formed. The total amount of "oxygenates", however, is still quite small when compared to that of the entire sample. This was confirmed by the results from a second NMR experiment. Fig. 7 illustrates more dramatically the power of class pre-separation. The bottom chromatogram is the retained fraction shown in Fig. 6 (bottom). The top chromatogram of the retained fraction resulted

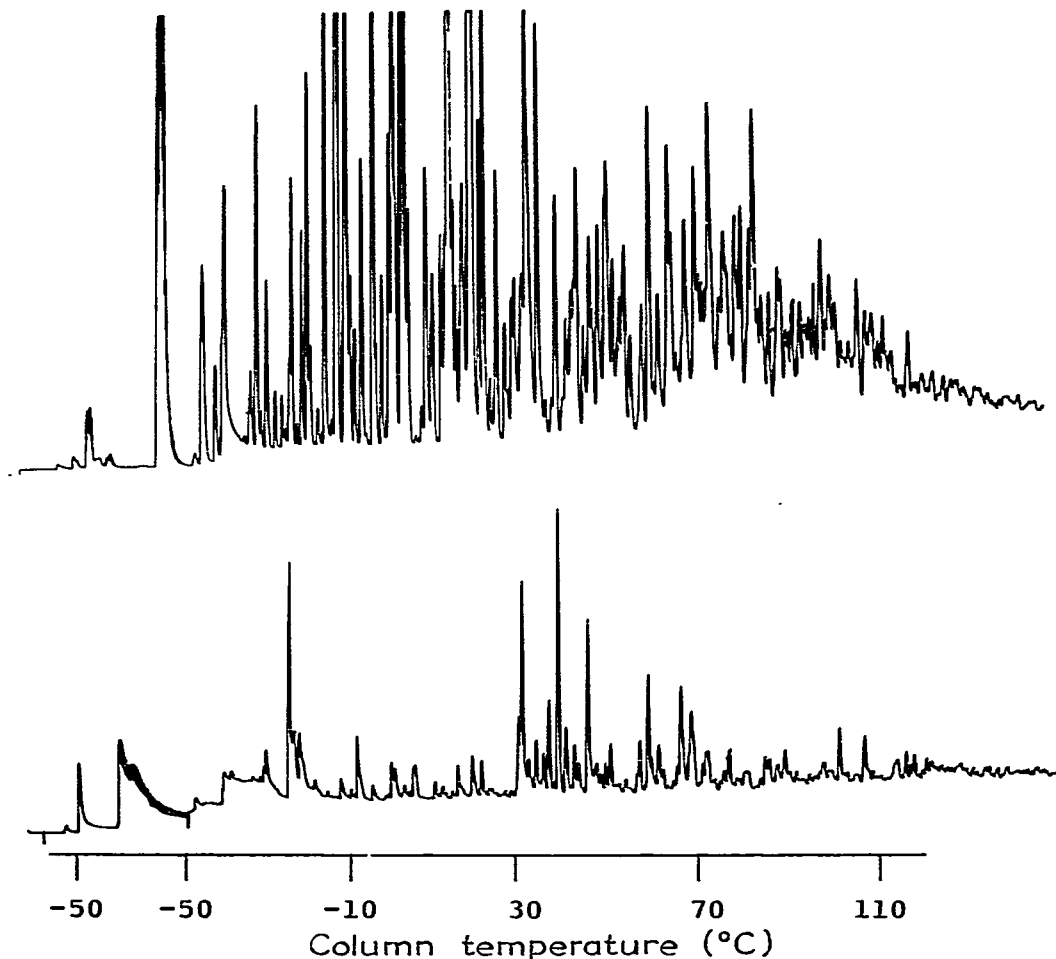


Fig. 6. Chromatograms showing the non-retained (top) and the retained fractions (bottom) obtained from the oxidatively degraded gasoline sample. Same analytical conditions as in Fig. 5.

when a sample 4.8 times larger was analyzed. In this experiment the bulk of the sample (the non-retained fraction) was not analyzed, but was allowed to flow out the vent of the system, after passing through the Eu sorbent. At the attenuation setting of the instrument it is clear that the non-retained constituents would have been well off-scale, perhaps overloading the capillary column and the detector. With the larger sample subjected to pre-fractionation, the chromatogram of the complexed fraction now shows the traces, with many identifiable peaks and easy to measure retention times. Samples of an identical concentrated oxygenate fraction were subsequently taken for GC-mass spectrometric (MS) analysis by directing the thermally desorbed sample out the vent of the sorbent system into a second clean Tenax trap. Both electron impact and chemical ionization MS methods were employed in order to identify compounds. For confirmation of identifications, the retention times of standard reference compounds were also matched in most instances. Table II lists the

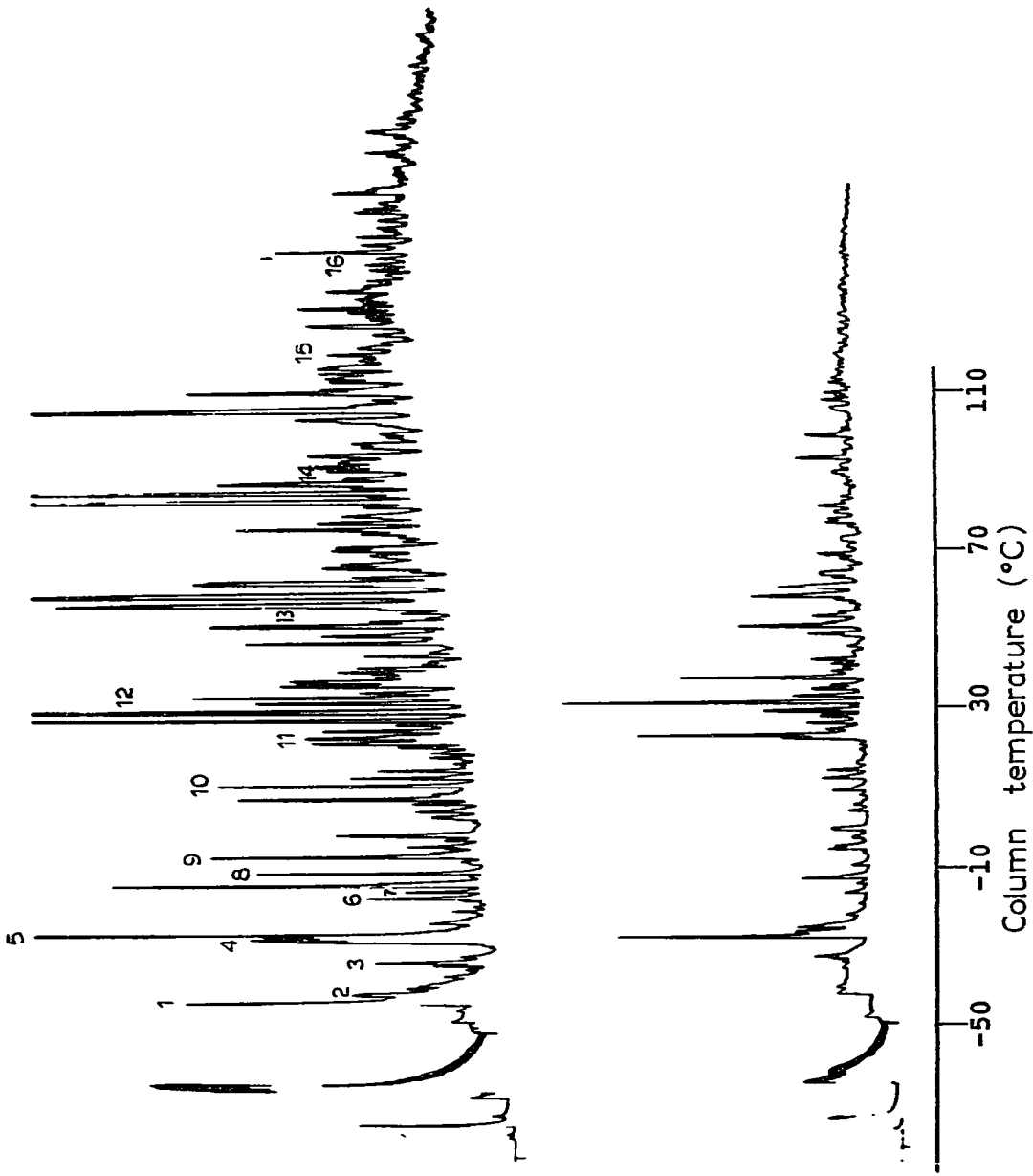


Fig. 7. Chromatograms showing analyses of the fraction of gasoline that had been partially degraded with oxygen. For comparison the bottom chromatogram is the one pictured at the bottom of the previous figure. The top chromatogram results when the amount subjected to analysis is increased by a factor of 4.8. Same conditions as in Fig. 5. Identifications are listed in Table II.

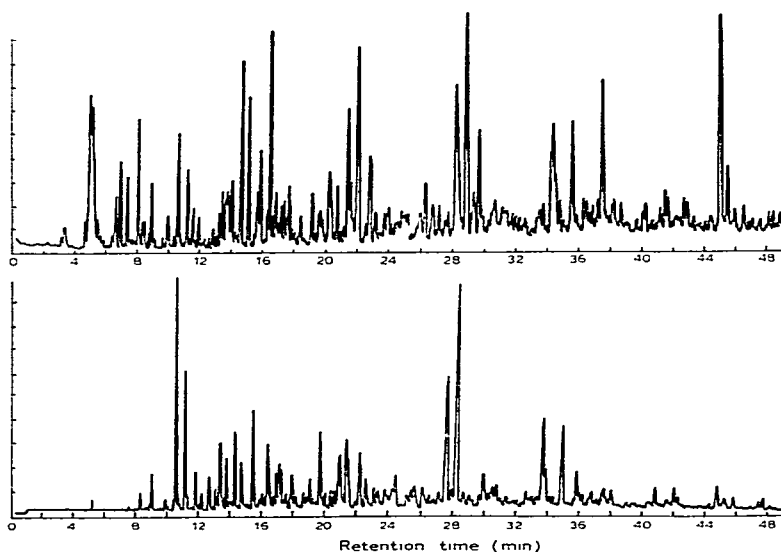


Fig. 8. Total ion chromatograms generated from the GC-MS analysis of the gasoline fraction pictured at the top of Fig. 7. The top trace is the ion chromatogram obtained from 70 eV electron impact MS using a Hewlett-Packard Model 5982A gas chromatograph-mass spectrometer, modified so that the fused silica capillary column extends into the ion source. The bottom trace is that obtained in the chemical ionization mode using isobutane as the reagent gas. Analytical conditions: 30 m  $\times$  0.31 mm SE-54 fused silica capillary column, He at 8 p.s.i.g., thermal focussing at  $-50^{\circ}\text{C}$ , then  $-50$  to  $-10^{\circ}\text{C}$  at  $8^{\circ}\text{C}/\text{min}$ , then  $-10$  to  $150^{\circ}\text{C}$  at  $2^{\circ}\text{C}/\text{min}$ .

compounds that were identified in the retained fraction. Fig. 8 shows the total ion chromatograms for the electron impact and chemical ionization analyses.

As expected, most of the compounds identified contain oxygen. They are the larger peaks in the chromatogram. Many of the unidentified compounds, present in lower concentrations, may be hydrocarbons. There are conceivable reasons for the presence of the hydrocarbons in the retained fraction. In the original sample the oxygenates were present as only a small fraction (*ca.* 1% at most) of the total. If only a small fraction of the hydrocarbons were retained by some non-ideal mechanism (*e.g.*, adsorption on active sites) this would be enough to show up in the chromatograms of the oxygenates. This does not seem to pose a serious problem, however, since the peaks are substantially smaller than the analytes of interest.

It is clear from these examples that one can use a selective sorbent containing lanthanide chelates to retain analytes that form complexes, and effectively pre-concentrate constituents, even if present at trace levels, while the bulk of the less interesting uncomplexed species (such as hydrocarbons) pass through the sorbent unretained. Conversely, one can also use complex formation on a selective lanthanide chelate sorbent to remove a relatively large amount of an uninteresting interfering nucleophilic solvent such as methanol or other major constituents of a sample while analyzing the unretained analytes, *e.g.*, hydrocarbons, chlorinated hydrocarbons. We also envision the use of lanthanide polymer sorbents as clean-up or "guard" pre-columns to protect analytical columns from degradation by highly polar compounds, many of which form complexes. By selective complexation it is possible to perform

analyses of many types of samples easier and with greater reliability than has heretofore been achievable.

#### ACKNOWLEDGEMENT

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