Prof. Robert E. Sievers
Department of Chemistry
University of Colorado Boulder, CO 80309

INNOVATIVE DETECTION, SEPARATION, AND SAMPLING TECHNIQUES FOR TRACE ANALYSIS BY GAS CHROMATOGRAPHY

1 October 1979 - 30 September 1983

AFOSR-80-0011

MAY 11 1984
REPORT DOCUMENTATION PAGE

1. REPORT NUMBER
   AFOSR-TR- 84-0384

2. GOVT. ACCESSION NO.
   A140944

3. REPORT DATE
   30Mar84

4. TITLE (and Subtitle)
   Innovative Detection, Separation, and Sampling Techniques for Trace Analysis by Gas Chromatography

5. TYPE OF REPORT & PERIOD COVERED
   Final Report: 1Oct79-30Sept83

6. PERFORMING ORG. REPORT NUMBER
   AFOSR 80-0011

7. AUTHOR(s)
   R. E. Sievers

8. CONTRACT OR GRANT NUMBER(s)
   R. E. Sievers AFOSR 80-0011

9. PERFORMING ORGANIZATION NAME AND ADDRESS
   Department of Chemistry, Box 215
   University of Colorado, Boulder, CO 80309.

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
    01109F  0303/Al

11. CONTROLLING OFFICE NAME AND ADDRESS
    Air Force Office of Scientific Research/NC
    Building 410
    Bolling AFB, DC 20332

12. REPORT DATE
    30Mar84

13. NUMBER OF PAGES
    5

14. MONITORING AGENCY NAME & ADDRESS (If different from Controlling Office)

15. SECURITY CLASS. (of this report)
    Unclassified

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)
    Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEYWORDS (Continue on reverse side if necessary and identify by block number)
   Gas Chromatography
   Selective Electron Capture Sensitization
   Chiral Separations
   Selective Sorbents
   Metal Chelates
   Microwave heating

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)
   Several studies related to sampling, separation and detection by gas chromatography have been concluded. Fundamental studies and practical applications have been made of selective electron capture sensitization in which the response of an electron capture detector is modified by addition of nitrous oxide to the carrier gas. Sizable signal enhancements have been observed for acetonitrile, acrylonitrile, acrolein, several amines, phenols and polycyclic aromatic hydrocarbons. A selective sorbent has been synthesized and developed that, when used as a chromatographic pre-column, selectively...
removes and concentrates oxygenates from a sample stream that also contains other organic compounds such as hydrocarbons and chlorinated hydrocarbons. A separation of a complex mixture of metal chelates has been accomplished using a bonded-phase, wall-coated fused silica capillary chromatographic column. Limited success has resulted from attempts to separate optical isomers when a chiral metal chelate is incorporated into a chromatographic stationary phase.
Innovative Detection, Separation, and Sampling Techniques for Trace Analysis by Gas Chromatography

The primary objectives of the research originally proposed under Grant No. AFOSR 80-0011 are presented below.

- Continuation of the development and study of selective electron capture sensitization (SECS) as a means to perform highly sensitive measurements of compounds that generally are not amenable to electron capture detection.
- Pre-analysis separation of complex mixtures using a serial sorbent sample collection system.
- Studies of chromatographic columns using lanthanide metal chelates including chiral chelates as a means to separate optical isomers.
- Studies of microwave heating in chromatographic systems.

Information in this final report presents the results and conclusions of this research.

Selective Electron Capture Sensitization (SECS)

Additional progress has been made in understanding and eliminating response peculiarities observed with a N\textsubscript{2}O-SECS system (1,4,5). Several problems associated with SECS are eliminated by carefully purifying the gases employed in the system. Various gas purifying schemes have been used and a suitable purifying agent has been found that results in reproducible behavior of the system.

Various classes of organic compounds have been studied using SECS. Sizable signal enhancements have been recorded for acetonitrile, acrylonitrile, acrolein, and various amines, phenols, and polycyclic aromatic hydrocarbons (5). The technique was used to aid in the identification of phenolic compounds in a complex wastewater fraction (5). A method for the trace analysis of vinyl chloride has also been developed using SECS (1).

Large differences in response have been found for closely related isomers of amines. These differences could be exploited to positively identify isomers which cannot be identified by other techniques such as mass spectroscopy.

The SECS technique is now being used routinely by other groups. Scientists at the NOAA Aeronomy Laboratory, Boulder, Colorado, our collaborators on the initial development of SECS, use the technique to monitor CO concentrations in ambient air. We have helped Dr. Randolph Ware, a geophysicist colleague at the Cooperative Institute for Research in Environmental Sciences at the University of Colorado, to use SECS to monitor \textsubscript{H}\textsubscript{2} concentrations in soil gases along earthquake fault zones.

Selective Sorbents

A novel bis(\beta-diketone), H\textsubscript{6}dihed, \textsubscript{[p-di(4,4,5,5,6,6,6-heptafluoro-1,3-hexanedionyl)benzene]} has been synthesized. This compound has the ability to form coordination polymers with the lanthanides. The polymers retain the excellent Lewis acidity characteristics of previously synthesized fluorinated tris(\beta-diketonates), yet are extremely non-volatile and consequently more suitable for use as stationary phases in gas chromatography. 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, tobacco smoke, urine and gasoline (2,3). In each case a separation into two fractions was accomplished, producing simplified chromatograms. The net result has facilitated identification of organic compounds by mass spectral and retention time matching techniques. Based on these tests with a variety of sample types containing highly complex mixtures, it can be concluded that this is a highly promising general analytical strategy.

Lanthanide β-diketonates have been successfully bonded to styrene-divinylbenzene copolymers. This sorbent has been characterized and used in the analyses of oxygenated species in the atmosphere. Preliminary experiments have also been performed using N,N-ethylenediamine(salicidieniminato)cobalt(II), Co(salen), coated on glass beads. This compound shows selectivity for the retention of Lewis bases containing nitrogen such as pyridine and methylpyridines.

The development of a selective sorbent for olefinic compounds has not been successful. Neither Rh(facam)(CO)₂, where facam is trifluoroacetyl-d-camphorate, nor Ag(hfa), where hfa is 1,1,5,5,5-hexafluoro-2,4-pentanedionate, retained any of the olefins passed over a bed of the complex that had been dissolved in a liquid phase and coated on a solid support. Many Pd complexes have also been studied. Although olefins can be retarded in the GC analysis, the interaction does not appear to be strong enough to quantitatively trap target compounds for later desorption and analysis. During the course of this study, however, an improved procedure has been discovered for the synthesis of di(o-phenylenebisdimethylarsine)-palladium(II)dichloride and dichloro-o-phenylenebisdimethylarsinepalladium(II).

Chromatography with Metal Chelates

A mixture of synthesized mixed ligand Cr(III) complexes was studied by GC/MS (7). The mixture was made from an equimolar solution of Cr(III), H₃f₃a (1,1,5,5,5-hexafluoro-2,4-pentanedione), H₃f₅a (1,1,1-trifluoro-2,4-pentanedione), and H₃f₉d (2,2-dimethyl-6,6,7,7,8,8,8-heptafluoro-3,5-octanedione). Of the 25 possible products, 24 were resolved using a fused silica capillary GC column. Mass spectrometric detection led to facile assignment of identities of the complexes and yielded information concerning gas phase stabilities.

A number of metal chelates with a new ligand, 2,2,7-trimethyloctane-3,5-dione, H₃f₉d, have been investigated for their use in gas and liquid chromatographic separations of transition metals (8). Cr(tod)₃ shows extraordinary stability in gas chromatographic columns at temperatures high enough to produce reasonably rapid elution. Cr(tod)₃ and Co(tod)₃ form geometrical isomers which can be separated on a reversed-phase analytical HPLC column using acetonitrile and water as eluents. Ni(tod)₂·MeOH, VO(tod)₂, and Hg(tod)₂ have been synthesized and the properties of these new compounds studied. These metal chelates and the isomers of the more stereochemically rigid complexes have been characterized by thermal gravimetric analysis, mass spectrometry, and, in the case of the diamagnetic Co(tod)₃, by nuclear magnetic resonance spectrometry. Additionally, the separation of all the geometrical isomers in a mixture of Cr(tfa)₃, Cr(fod)₃, and Cr(tod)₃ was accomplished in a single HPLC experiment.
The symmetrical hexadentate ligand, \(1,1,1\)-tris-(2-oxo-9,9,9-trifluoro-6,8-nanonanedione)ethane (H\(\text{stfne}\)), has been synthesized. The synthesis of the Co(II), Co(III), Fe(III), Eu(III) and Yb(III) complexes with H\(\text{stfne}\) has been investigated, but characterization of the complexes has proven difficult.

The use of chiral lanthanide metal chelates in gas chromatographic stationary phases has resulted in limited success. A stationary phase containing Eu(III)(facam)\(_3\) was able to partially resolve the isomers of epoxypropane.

**Microwave Heating in Chromatographic Systems**

Several attempts were made to use selective microwave heating in chromatographic systems, with limited success. The first involved the selective heating of a microwave-absorbing liquid phase (TCEP) coated on Chromosorb W. Some changes were seen in the separation of six test compounds, but it has been difficult to regulate and predict the effects of microwave radiation on other chromatographic separations.

**Written Publications in Journals and Books**


**Presentations (Presented by author in boldface)**

"Stereochemistry of Metal $\beta$-Diketonates", R. E. Sievers, Chemistry Dept. Seminars, Universite de Nice and Universite de Montpelier, France (Oct. 5, 6, 1981).


"Studies of Complex Mixtures of Tris($\beta$diketonato)chromium(III) Geometrical..."

Senior Research Personnel

Dr. R. M. Barkley
Dr. K. C. Brooks
Dr. J. B. B. Heynes
Dr. C. A. Koval
Dr. R. W. Siergiej
Dr. S. Singhawangcha
Dr. B. Wenclawiak

Junior Research Personnel

M. K. Conditt
J. DeAngelis
J. N. Gillis
R. C. Greaves
S. D. Harvey
S. B. Hawthorne
A. J. Hills
R. S. Hutte
B. A. Medeiros
S. A. Nyarady
M. P. Phillips
J. E. Picker
K. W. Sigvardson
S. W. Stiller
E. J. Williams
M. A. Wizner

Advanced Degrees

The following received advanced degrees under partial sponsorship of AFOSR Grant No. 800011:

K. C. Brooks, Ph. D., 1981, "NMR Lanthanide Shift Reagents with Polydentate Cage Ligands and the Gas Chromatographic Separation of Tris(β-diketonato)chromium(III) Geometrical Isomers with Fused Silica Capillary Columns".

S. D. Harvey, M.B.S., 1981, "Concentration Profile of Volatile Organics in the Atmosphere During a Twenty-four Hour Period".


J. E. Picker, Ph. D., 1981, "The Use of Lanthanide Chelates as Selective Complexing Sorbents for Gas Chromatography".

E. J. Williams, Ph. D., 1984, "Metal Beta-Diketonate Chelates as Emissions-Reducing Fuel Additives and a Lanthanide Containing Polymeric Selective Sorbent".

M. A. Wizner, Ph. D., 1981, "Determination of Compound Responses to a Sensitized Electron Capture Detector".