

Note

Application of metal β -diketonate polymers as selective sorbents in complex mixture analysis and for sulfur-containing compounds

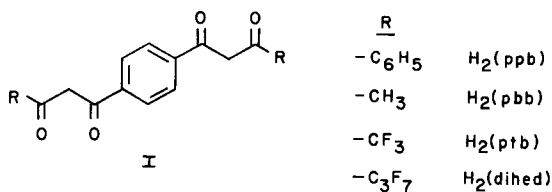
THOMAS J. WENZEL***, PHILIP J. BONASIA and THOMAS BREWITT

Department of Chemistry, Bates College, Lewiston, ME 04240 (U.S.A.)

(First received September 7th, 1988; revised manuscript received November 14th, 1988)

The number of volatile constituents in most environmental and biological samples precludes the ability to completely resolve all of the components using gas chromatography (GC). Computer methods are available for deconvoluting overlapping peaks in the chromatogram¹⁻³. An alternative approach is to simplify the chromatogram through the use of one or more selective sorbents. Any material that can selectively retain certain compounds from a gaseous mixture, while allowing other compounds to pass through unretained, can serve as a selective sorbent for GC. It is desirable to utilize selective sorbents that exhibit adsorption that is reversible with temperature⁴⁻⁸. In this case, the sorbent need only be heated to remove adsorbed compounds.

In a previous report, metal β -diketonate polymers of Ni(II), Cu(II), Zn(II) and La(III) were evaluated as selective sorbents for GC⁸. The ligands used to prepare the metal complexes are bis- β -diketones of structure I. The orientation of the β -diketone



units on the aromatic ring are such that polymeric materials result from the synthesis of metal complexes. The polymers are non-volatile and most are thermally stable. The metal ions in the polymers are coordinatively unsaturated and can form adduct complexes with suitable Lewis bases. The equilibrium constant for adduct formation depends on electronic and steric effects of the donor, the identity of the metal ion, the substituent group of the ligand, and temperature⁸.

La(III) and Ni(II) exhibited the greatest retention of oxygen- and nitrogen-containing compounds, Zn(II) and Cu(II) the least. Polymers with the C₃F₇ substituent group, the most electron withdrawing of those studied, exhibited the greatest

* On leave, in 1989 at the Department of Chemistry, Paul Gross Laboratory, Duke University, Durham, NC 27706, U.S.A.

retention of oxygen- and nitrogen-containing compounds. Polymers with the C_6H_5 substituent group exhibited the least retention. The following series of four sorbents was identified as that which offered the widest degree of selectivity with regard to retention of hard Lewis bases: $Zn(ppb) > Cu(dihed) > La(pbb) > La(dihed)$.

In this report we demonstrate the application of this series of four sorbents in the analysis of complex mixtures. The sorbent series can be used to divide a mixture with one complex chromatogram into five simpler chromatograms. The use of $Ag(I)$ and $Ni(II)$ bis- β -diketonates as sorbents for sulfur-containing compounds is also described.

EXPERIMENTAL

Preparation of $Ag_2(dihed)$

The ligand $H_2(dihed)$ was synthesized as previously described⁴. The complex with silver was prepared by a modification of a literature method⁹. To 1 g (0.0018 mol) of $H_2(dihed)$ dissolved in 40 ml of methanol 0.9 ml of 4 *M* sodium hydroxide (0.0036 mol) was added. The solution was stirred vigorously and a solution of silver nitrate (0.61 g, 0.0036 mol) in 20 ml of distilled water was added. The resulting mixture was stirred for 30 min after which the brown solid was collected by suction filtration. The solid was dried for 24 h *in vacuo* over P_4O_{10} . The material decomposed over the range from 156 to 180°C. Anal. calc. for $Ag_2C_{18}H_6O_4F_{14}$: C, 28.15; H, 0.79. Found: C, 27.76; H, 0.99.

Preparation of pre-columns containing the metal polymers

Pre-columns containing the $La(dihed)$, $La(pbb)$, $Cu(dihed)$, $Ni(dihed)$, $Ni(ppb)$ and $Zn(ppb)$ polymers were prepared as previously described⁸. A pre-column containing $Ag_2(dihed)$ was prepared using an analogous procedure. Gas Chrom Z 80–100 mesh (Applied Science) was first coated with a layer of 3% SE-30. A 3% loading of the $Ag_2(dihed)$ was then applied. The metal complex was dissolved in methanol for the coating step. Since silver β -diketonates are slightly light sensitive, all glassware employed in the manipulations of the silver complex were covered with aluminum foil. The coated support was packed into a 25 cm \times 2.2 mm I.D. pre-column (Valco). The sorbent was conditioned at 140°C under a flow of nitrogen gas for 30 min.

Apparatus and procedures

The valve system with sorbent pre-columns and gas chromatograph were as previously described⁸. Chromatograms were run on a 25-m cross-linked 5% phenyl methyl silicone fused-silica capillary column (Hewlett-Packard) at a flow-rate of 1 ml/min. Nitrogen was employed as the carrier gas. Procedures for employing and testing the sorbents were as previously described⁸.

Samples of cigarette smoke were obtained by drawing smoke for a set period of time (usually 5 s) from the end of a cigarette through a trap containing Tenax GC. The volatile constituents of urine were obtained by placing 90 ml of urine in a three-necked flask fitted with helium inlet, thermometer and reflux condenser. The outlet of the reflux condenser was adapted to accommodate a sorbent containing Tenax GC. The sample was stirred and maintained at 67–70°C for 1 h. During this time the head space in the flask was continually swept with helium (30 ml/min).

RESULTS AND DISCUSSION

The utility of the sorbent series in the analysis of complex mixtures was demonstrated with cigarette smoke and urine. The results with cigarette smoke are shown in Fig. 1. Fig. 1a is the chromatogram of those compounds retained by Zn(ppb). The compounds unretained by the Zn(ppb) were then passed through a sorbent containing Cu(dihed). The chromatograms in Fig. 1b-d are of those compounds retained by the Cu(dihed), La(ppb) and La(dihed) sorbents respectively. The chromatogram in Fig. 1e is for those compounds unretained by the series of sorbents.

One trend in the series of chromatograms is that the compounds retained by each sorbent tend to cluster according to volatility. The majority of the compounds retained by Zn(ppb) are in the latter part of the chromatogram, and are therefore the less volatile Lewis bases in the sample. The peak shapes for early eluting compounds in this chromatogram exhibit tailing, which is indicative of highly polar compounds such as amines or alcohols. These two classes of compounds exhibit large association constants with metal β -diketonate complexes^{8,10,11}, and it is not surprising that they might be retained on the most selective sorbent of the series. A general progression

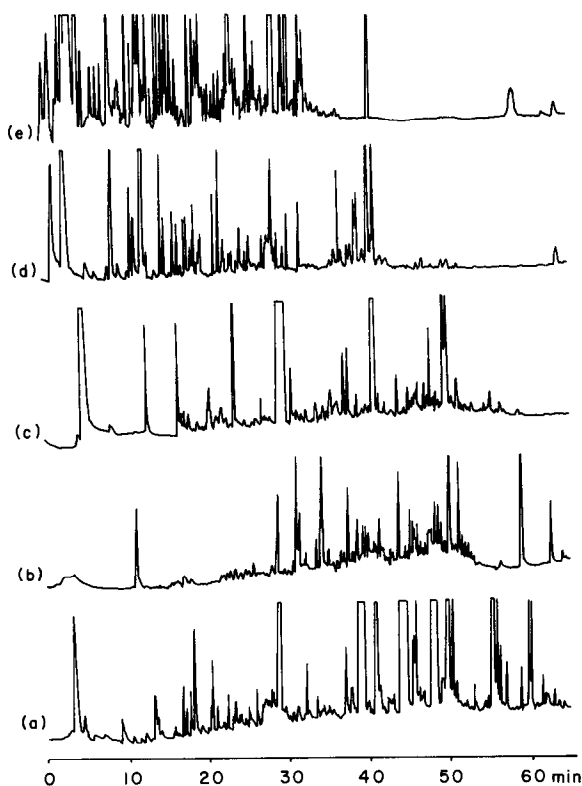


Fig. 1. Chromatograms of the volatile constituents of cigarette smoke (a) retained by Zn(ppb) at 100°C, (b) retained by Cu(dihed) at 100°C, (c) retained by La(ppb) at 100°C, (d) retained by La(dihed) at 100°C, and (e) unretained. Thermally focussed at -50°C for 5 min and then 3°C/min to 150°C. See Experimental section for column and sorbent description.

from less to more volatile constituents is observed for the chromatograms of the compounds retained by Cu(dihed), La(pbb) and La(dihed). The compounds unre- tained by the sorbent series elute in the earlier portion of the chromatogram and are therefore the more volatile components of the sample. The chromatograms obtained for cigarette smoke using the sorbent series were reproducible over a six-week period of analysis. Furthermore, the intensities of the peaks in the individual chromatograms were directly dependent upon the sampling time, and hence sample size.

The chromatograms obtained for the volatile constituents of urine are shown in Fig. 2. Although not as pronounced as with cigarette smoke, a general trend in the volatilities of the compounds retained by each sorbent is observed. The use of this four-sorbent series allows for the conversion of one complex chromatogram into five simpler chromatograms. Alternatively, the analysis of certain "target" compounds is facilitated. In the latter case, one need only analyze the sorbent, or sorbents, on which the target compounds are retained. All other fractions can be vented without analysis. Sorbents have been used for periods of several months with no observed change in performance.

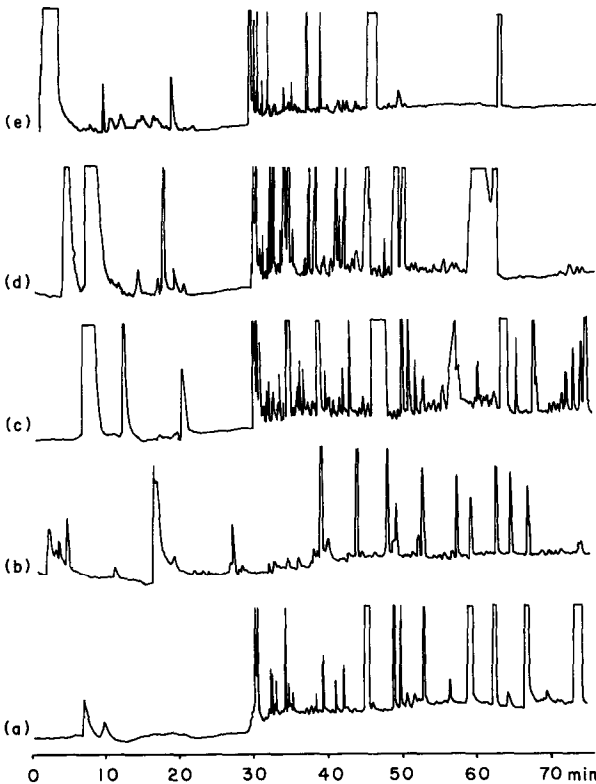


Fig. 2. Chromatograms of the volatile constituents of urine (a) retained by Zn(ppb) at 100°C, (b) retained by Cu(dihed) at 100°C, (c) retained by La(pbb) at 100°C, (d) retained by La(dihed) at 100°C, and (e) unre- tained. Thermally focussed at -50°C for five min and then $2^{\circ}\text{C}/\text{min}$ to 100°C . See Experimental section for column and sorbent description.

Sorbent studies on sulfur-containing compounds:

The complexes $\text{Ag}_2(\text{dihed})$, $\text{Ni}(\text{dihed})$ and $\text{Ni}(\text{pbb})$ were tested for their ability to retain sulfur-containing compounds. $\text{Ag}(\text{I})^{12}$ and nickel β -diketonates¹³ are known to form adduct complexes with sulfur-containing compounds. Sulfur-containing compounds such as methanethiol can be selectively adsorbed on mercury salts such as mercuric acetate¹⁴. Removal of the thiol requires treatment with hydrochloric acid followed by extraction into an organic solvent. General sorbents such as Tenax GC and XAD resins have also been evaluated for their ability to retain sulfur-containing compounds¹⁵. Thiophene, tetrahydrothiophene, di-*n*-butyl sulfide and straight-chain thiols (C_5 – C_8) were used as model substrates to test the sorbent properties of the metal β -diketonate polymers.

At 100°C, thiophene was not retained by any of the sorbents. This is not surprising since the conjugated ring system in thiophene is expected to reduce the basicity of the sulfur atom, much the same as is observed with furan and tetrahydrofuran^{4,16}. All of the other compounds were completely retained by $\text{Ag}_2(\text{dihed})$ and $\text{Ni}(\text{dihed})$ at 100°C. The retention of these compounds by $\text{Ag}_2(\text{dihed})$, however, was irreversible at desorption temperatures of 130 and 140°C. This irreversible adsorption may well be the result of strong complexation between silver and sulfur-containing compounds¹². A temperature of 140°C was judged as the upper limit for $\text{Ag}_2(\text{dihed})$ because of the decomposition that starts to occur at about 156°C. The retention of tetrahydrothiophene, di-*n*-butyl sulfide, and the straight chain thiols by $\text{Ni}(\text{dihed})$ was irreversible at desorption temperatures of 150°C. At 170°C, only tetrahydrothiophene was desorbed from $\text{Ni}(\text{dihed})$.

At 100°C, $\text{Ni}(\text{pbb})$ exhibited partial retention of tetrahydrothiophene (98%) and di-*n*-butyl sulfide (66%), and complete retention of the straight chain thiols. Tetrahydrothiophene, di-*n*-butyl sulfide and the C_5 thiol were successfully desorbed at 150°C, whereas the C_6 – C_8 thiols were not. The C_6 – C_8 thiols were desorbed, however, at 170°C. The recovery of the sulfur-containing compounds from $\text{Ni}(\text{pbb})$ was assessed by comparing the integrated areas of the peaks in the chromatogram of the retained compounds to those obtained in the direct injection of the same sample. For each compound, the areas were essentially identical and complete recovery was indicated. Of the sorbents we tested, $\text{Ni}(\text{pbb})$, by virtue of its reversible adsorption, appears to be the best choice for sulfur-containing compounds.

ACKNOWLEDGEMENTS

We would like to thank the Petroleum Research Fund and the National Science Foundation (Two- and Four-Year College Science Instrumentation Program) for supporting this work.

REFERENCES

- 1 G. H. Rayborn, G. M. Wood, Jr., B. T. Upchurch and S. J. Howard, *Am. Lab. (Fairfield, Conn.)*, 18 (1986) 56.
- 2 S. C. Gates, M. J. Smisko, C. L. Ashendel, N. D. Young, J. F. Holland and C. C. Sweeley, *Anal. Chem.*, 50 (1978) 433.
- 3 R. G. Dromey, M. J. Stefik, T. C. Rindfleisch and A. M. Duffield, *Anal. Chem.*, 48 (1976) 1368.
- 4 J. E. Picker and R. E. Sievers, *J. Chromatogr.*, 203 (1981) 29.

- 5 J. E. Picker and R. E. Sievers, *J. Chromatogr.*, 217 (1981) 275.
- 6 E. G. Boeren, R. Beijersbergen van Henegouwen, I. Bos and T. H. Gerner, *J. Chromatogr.*, 349 (1985) 377.
- 7 E. J. Williams and R. E. Sievers, *Anal. Chem.*, 56 (1984) 2523.
- 8 T. J. Wenzel, L. W. Yarmaloff, L. Y. St. Cyr., L. J. O'Meara, M. Donatelli and R. W. Bauer, *J. Chromatogr.*, 396 (1987) 51.
- 9 T. J. Wenzel and R. E. Sievers, *Anal. Chem.*, 53 (1981) 393.
- 10 J. K. M. Sanders and D. H. Williams, *J. Am. Chem. Soc.*, 93 (1971) 641.
- 11 R. T. Pflaum and L. E. Cook, *J. Chromatogr.*, 50 (1970) 120.
- 12 H. Sigel, K. H. Scheller, V. M. Rheinberger and B. E. Fischer, *J. Chem. Soc., Dalton Trans.*, (1980) 1022.
- 13 V. Schurig and W. Burkle, *J. Am. Chem. Soc.*, 104 (1982) 7573.
- 14 R. Knarr and S. M. Rappaport, *Anal. Chem.*, 52 (1980) 733.
- 15 A. Przyjazny, *J. Chromatogr.*, 333 (1985) 327.
- 16 R. E. Rondeau and R. E. Sievers, *Anal. Chem.*, 45 (1973) 2145.