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Supercritical fluid extraction of metal-containing selective sorbents

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ABSTRACT

Nickel(II), copper(II), zinc(II) and lanthanum(III) complexes with bis-β-diketonate ligands form polymeric materials that function as selective sorbents for use as gas chromatographic precolumns. Supercritical fluid extraction was evaluated as a method of desorbing compounds retained by these sorbents. Alcohols, ketones, esters and sulfur-containing compounds were effectively extracted using carbon dioxide at 80 atm (1 atm = 101 325 Pa) and 50°C. The blanks observed with supercritical fluid extraction were often better than those obtained with thermal desorption. The applicability of supercritical fluid extraction is demonstrated on the constituents of cigarette smoke retained on a copper-containing sorbent. Two other sorbents employing metal complexes of either a β-diketone derivative of polystyrene or a β-ketoamide derivative of silica gel were evaluated. The blanks with these materials were not found to be suitable using either thermal desorption or supercritical fluid extraction.

INTRODUCTION

Gas chromatography is the method of choice for analyzing volatile constituents of samples. The large number of volatile compounds in many samples, however, often results in complex chromatograms with overlapping peaks. One approach to reducing the complexity of gas chromatograms is to employ selective detectors. Another is to use selective sorbents in the sample collection or workup prior to analysis. Selective sorbents are designed to retain only specific compounds from a sample mixture. In most instances it is desirable to be able to remove the compounds retained by the sorbent for analysis. This has usually been accomplished by thermal desorption, however, the technique of supercritical fluid extraction has increasingly been applied as a desorption method [1–9].

Carbon dioxide is usually employed in the supercritical fluid extraction of sorbent materials. Supercritical carbon dioxide is relatively inert, a property which facilitates the design of extraction devices, the handling of the effluent, and reduces the likelihood of degradation of the sorbent polymer. The low critical point conditions of carbon dioxide [73 atm (1 atm = 101 325 Pa), 31°C] contribute to the ease of construction of an extraction apparatus, and reduce the possibility of thermal degradation of the sorbent polymer. Supercritical carbon dioxide is nonpolar, which may limit its use in applications when highly polar molecules are to be extracted. Its polarity can be raised by elevating the pressure and decreasing the temperature of the system [10]. At temperatures of approximately 50°C and pressures of approximately 2200 atm the Hildebrand solubility parameter is similar to that of methylene chloride [10]. It is also possible to add polar modifiers such as methanol, acetonitrile, or water to the carbon dioxide to increase

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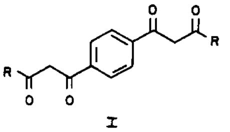
the polarity [9,11]. Supercritical fluid extraction of sorbents can be performed in either an off- or on-line [11–15] mode.

We have developed a series of metal-containing selective sorbents based on complexes with bis-β-diketone ligands of structure **I** [16,17].



I

R	
$-C_6H_5$	H_2(ppb)
$-CH_3$	H_2(pbb)
$-CF_3$	H_2(ptb)
$-C_3F_7$	H_2(dihed)

The orientation of the β-diketone groups is such that metal complexes of **I** form polymers, an example of which is shown in Fig. 1. Nickel(II), zinc(II), copper(II) and lanthanum(III) were chosen for study because β-diketonate complexes of these metals are coordinatively unsaturated, and these metals span a range of Lewis acidities. Metal complexes of **I** are therefore effective sorbents for Lewis bases such as oxygen-, nitrogen- and sulfur-containing compounds [16,17]. The selectivity of the sorbents varies depending on the metal and the substituent group of the β-diketone ligand. Electron-withdrawing moieties such as trifluoromethyl and heptafluoropropyl groups enhance the Lewis acidity of the metal and increase the association constants with Lewis bases. Electron-donating moieties such as phenyl and methyl groups do the opposite. A series of four sorbents that provide the optimum range of selectivity has been described [17].

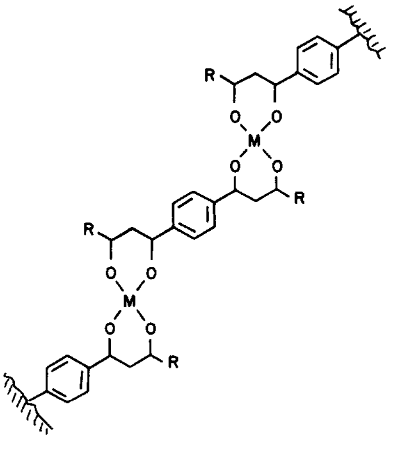


Fig. 1. Structure of the β-diketonate polymer for a metal in the 2+ oxidation state.

Previous work on metal-containing sorbents utilized thermal desorption [16–20]. We now describe the use of supercritical fluid extraction with these sorbents. Supercritical fluid extraction with carbon dioxide will be shown to be an effective means of removing compounds retained by these sorbents. Supercritical fluid extraction was also tested with Eu(III) and Cu(II) complexes of a β-diketone-derivatized polystyrene described by Williams and Sievers [20]. Repeated clogging of the restrictor on the extraction device seemed to indicate that these polystyrene derivatives were slightly soluble in supercritical carbon dioxide. The Cu(II) complex of a β-ketoamide derivative of silica gel was also evaluated as a selective sorbent, however, adequate blanks could not be obtained using either thermal desorption or supercritical fluid extraction.

EXPERIMENTAL

Reagents

Chemicals employed in the synthetic preparations were reagent grade and were used as received. Solvents were dried prior to use. Tenax GC (20–35 mesh) and Chromosorb 102 (60–80 mesh) were obtained from Alltech (Deerfield, IL, USA). Supercritical fluid-grade carbon dioxide was obtained from Scott Specialty Gases (Plumsteadville, PA, USA).

Preparation of polymer sorbents

Metal polymers of **I** were prepared as previously described [16]. The 4,4,4-trifluoro-1,3-butanedionyl derivative of Chromosorb 102 (**II**), and europium(III) complex of **II** were prepared as reported by Williams and Sievers [20]. Spectral and elemental analysis confirmed the identity of the desired products. The copper(II) complex of **II** was prepared by filtering a hot solution of cupric acetate (1.68 g) in 60 ml of water through a fine-pore sintered glass crucible into an Erlenmeyer flask containing a stirred suspension of **II** (2.0 g) in 60 ml of ethanol. The polymer immediately turned green upon the addition of the copper solution. The flask was stoppered and shaken on an orbital shaker for 5 h, after which the solid was collected by suction filtration and washed with copious amounts of water and 95% aqueous ethanol. The product was dried under vacuum in a desiccator for 12 h. Elemental analysis (Galbraith Labs., Knoxville, TN, USA) showed the product to contain 2.97% copper. This value is reasonable assuming that 8–10% of the styrene rings are derivatized with the β-diketone group [20].

The synthesis of the 4,4,5,5,6,6,6-heptafluoro-1,3-hexanedionyl derivative of Chromosorb 102 was attempted by a procedure analogous to that used to prepare the trifluoro derivative. A spot test using a solution of iron(III) chloride failed to show much incorporation of β-diketone moieties onto the polymer. Similar attempts to prepare the 1,3-butanedionyl derivative also failed to produce the desired product as evidenced by testing with iron(III) chloride.

A β-ketoamide derivative of silica gel (**III**) was prepared by reacting diketene with aminopropyl-derivatized silica according to previous methods [21]. The Cu(II) complex was prepared by a procedure analogous to that described above for the polystyrene except that the copper(II) acetate was added in hot methanol. Elemental analysis (Galbraith Labs.) showed the product to contain 1.00% copper.

Precolumns

Precolumns [10 × 1/8 in. I.D. (1 in. = 2.54 cm) rapid heating/cooling, Valco, Houston, TX, USA] containing La(dihed), Ni(dihed), Cu(dihed), and Zn(ppb) were prepared and conditioned as previously described [16]. The Cu(II) and Eu(III) complexes of **II** were packed by plugging one end of the precolumn with glass wool and attaching that end to a vacuum pump. The polymer was added under suction, the other end plugged with glass wool, and then the trap was conditioned either thermally or by repeated extraction with supercritical carbon dioxide. The Cu(II) and complex of **III** was packed by procedures similar to complexes of **I** [16] and conditioned thermally at 100°C for repeated intervals, or by repeated extraction with supercritical fluid carbon dioxide.

Apparatus and procedures

The valve system with sorbent precolumns was as previously described [16]. Chromatograms were obtained on either a Hewlett-Packard 5880 gas chromatograph with flame ionization detector or Hewlett-Packard 5890 gas chromatograph with mass-selective detector. The column was a 25-m cross-linked 5% phenyl methyl silicone fused-silica capillary column (Hewlett-Packard), and the flow-rate was 1 ml/min. Helium or nitrogen was employed as the carrier gas.

A diagram of the apparatus used for supercritical fluid extraction is shown in Fig. 2. A syringe pump (Model 260D; ISCO, Lincoln, NE, USA) was fitted with a carbon dioxide-delivery system and shut off valves both before and after the syringe. The metal-containing trap was connected to the outlet valve of the syringe pump via a 30 in. length of 1/16 in. O.D. stainless-steel tubing. Supercritical conditions were maintained in the metal-containing trap by connecting an uncoated 4 in. length of 20 μm I.D. fused-silica restrictor (Polymicro Technologies, Phoenix, AZ, USA) to the end of the trap. The end of the restrictor was either immersed in 2 ml of methylene chloride or connected to a trap containing Tenax GC, either of which were maintained at ambient temperatures.

The chamber was filled with carbon dioxide, the valves closed, and the chamber then pressurized to the desired value. The outlet valve was then opened and when the flow-rate had

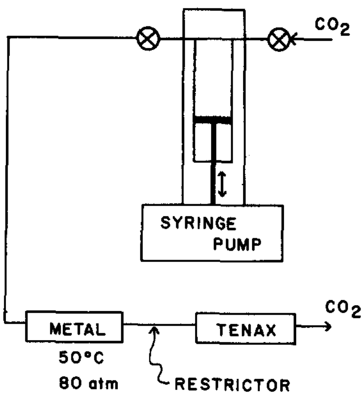


Fig. 2. Diagram of the apparatus for supercritical fluid extraction.

stabilized, which required only several seconds, the metal-containing sorbent trap was heated above the critical temperature for the desired length of time. After completion of the extraction step, the contents of the methylene chloride or Tenax trap were analyzed. Samples of ketones, esters, alcohols and sulfur-containing compounds were prepared by dissolving 1 μl of each compound in 5 ml of methanol. A 1-μl sample of the methanol solution was used for evaluating the sorbent properties as previously described [16].

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.

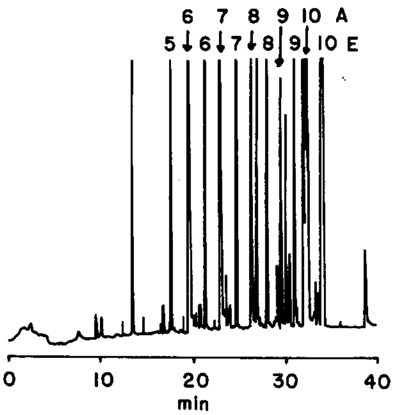


Fig. 3. Chromatograms of *n*-alcohols (6–10A = C_6–C_{10}) and methyl esters (5–10E = C_5–C_{10}) retained by La(dihed) at 100°C and desorbed via supercritical fluid extraction (80 atm, 50°C, 10 min).

RESULTS AND DISCUSSION

Preliminary investigation of the efficacy of using supercritical fluid extraction with metal-containing polymer sorbents was investigated using homologous series of 2-ketones, *n*-alcohols, and methyl esters with sorbent traps containing La(dihed), Cu(dihed) or Zn(ppb). In previous work with metal-containing sorbents with **I**, it was shown that oxygenated donor compounds associated most strongly with La(dihed) [16,17]. At temperatures of 100°C, the test ketones (C_5–C_{10}), esters (C_4–C_{10}) and alcohols (C_6–C_{10}) were fully retained by La(dihed). In Fig. 3 is shown the chromatogram of a sample of methyl esters and alcohols retained by La(dihed) and extracted in 10 min at 50°C and 80 atm. Even under these relatively mild conditions, the retained compounds are extracted. Comparison of the integrated areas of the peaks to those of the same sample when thermally desorbed directly from Tenax into the gas chromatograph indicate that the extraction and recovery of the compounds from the La(dihed) sorbent was complete. After completion of the supercritical fluid extraction, the La(dihed) was subjected to a 5 min thermal desorption at 150°C. The resulting chromatogram showed no peaks for any of the alcohols or methyl esters, confirming the efficiency of removal by supercritical fluid extraction. Similar efficiencies of removal were noted for the ketones, esters and alcohols on Cu(dihed) and Zn(ppb).

Two reasons might be proposed for the efficiency of extraction of these compounds from the metal-containing sorbents under the relatively mild conditions. The first is that all of the test solutes have aliphatic moieties that ought to enhance their solubility in the non-polar supercritical carbon dioxide. The second is that carbon dioxide may adsorb to the metal ions in the sorbents, thereby facilitating the desorption of the adsorbed solutes.

The volatile constituents of cigarette smoke were used to further evaluate supercritical fluid extraction of these sorbents. Portions of the chromatograms for total smoke, and the retained and unretained components of smoke after passage through Cu(dihed) are shown in Fig. 4. Only that portion in which peaks were observed in the chromatogram of the compounds retained by Cu(dihed) is shown. The chromatogram of the total smoke and those constituents unretained by Cu(dihed) are identical in many respects. The variations in relative intensity of several of the peaks was typical of the reproducibility of smoke from one analysis to the next. The major constituents in the chromatogram of the unretained compounds were identified as aromatic hydrocarbons. The peaks ob-

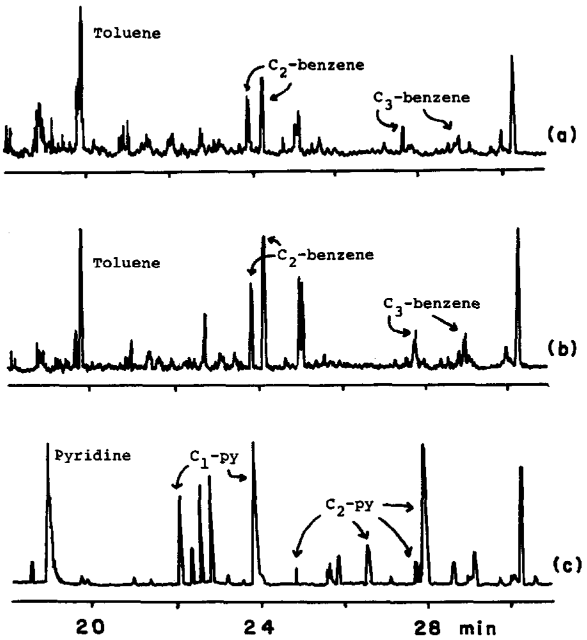


Fig. 4. Chromatograms of the volatile constituents of cigarette smoke: (a) total smoke, (b) unretained by Cu(dihed) at 100°C and (c) retained by Cu(dihed) at 100°C with desorption via supercritical fluid extraction (200 atm, 100°C, 20 min). py = Pyridine.

served in the chromatogram of those compounds retained by Cu(dihed) represent minor constituents in the total smoke, and primarily correspond to pyridine-containing compounds. Those compounds that were identified by mass spectral data are labelled in the chromatograms.

Removal of the pyridine-containing compounds from Cu(dihed) using supercritical fluid extraction was not complete at 80 atm and 50°C. Increasing the temperature, pressure, and extraction time were all observed to improve the extraction efficiency, as shown by the data in Table I. The efficiency of extraction was better for methyl pyridines than for pyridine. Complete removal of all of the adsorbed compounds except pyridine was effected at conditions of 200 atm, 100°C and 20 min extraction time.

An advantage of supercritical fluid extraction over thermal adsorption can be seen by comparing the blanks obtained using the two methods. The series of chromatograms shown in Fig. 5 for *n*-alcohols retained on Cu(dihed) illustrate this point. The chromatogram in Fig. 5a is that of the unretained alcohols. The C_6 alcohol is partially retained at 100°C; all of the other alcohols are fully retained at the conditions employed (100°C, 5 min). The chromatogram in Fig. 5b is that of the retained *n*-alcohols removed by supercritical fluid extraction. The extra peaks occurring in the latter portion of the chromatogram were noted when the sample was directly injected into the gas chromatograph and are therefore impurities in the alcohols. The chromatogram in Fig. 5c was obtained by thermal desorption of the polymer at 150°C immediately after completion of the supercritical fluid extraction. Of particular interest in this chromatogram are the five peaks at 8, 10, 16, 18 and 24 min. The intensity of these peaks increased with desorption temperature. They are believed to be thermal degradation products of the sorbent. These peaks were not observed to any significant extent in the chromatogram obtained after supercritical fluid extraction. The metal polymers of I also exhibit long-term stability under the conditions employed for the supercritical fluid extraction. One particular

TABLE I

EXTRACTION OF PYRIDINES FROM Cu(dihed)

Pressure (atm)	Temperature (°C)	Time (min)	Extraction (%)		
			Pyridine	C_1-pyridine	C_2-pyridine
120	50	10	29	96	77
120	50	20	33	99	98
120	100	20	53	100	100
200	100	20	89	100	100

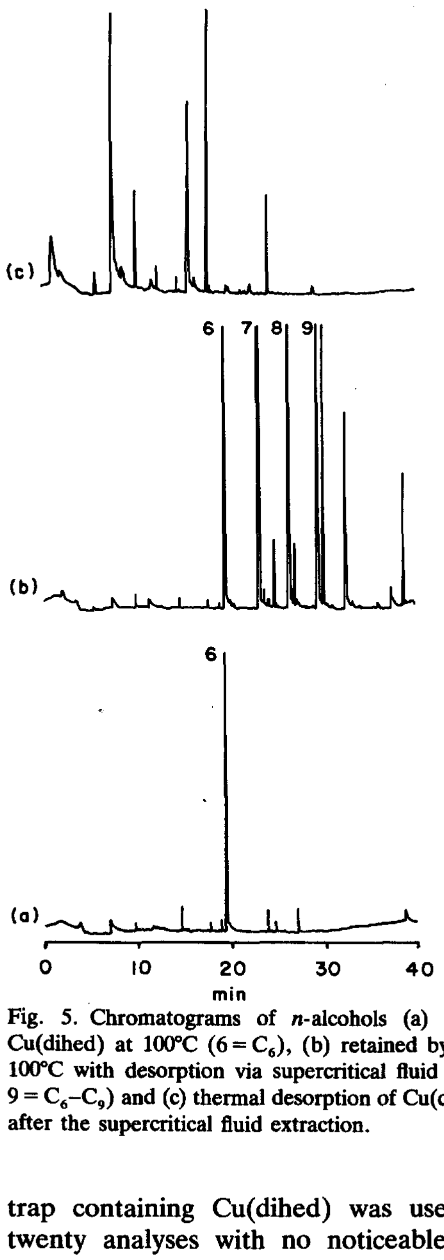


Fig. 5. Chromatograms of n-alcohols (a) unretained by Cu(dihed) at 100°C ($6 = C_6$), (b) retained by Cu(dihed) at 100°C with desorption via supercritical fluid extraction ($6–9 = C_6–C_9$) and (c) thermal desorption of Cu(dihed) at 150°C after the supercritical fluid extraction.

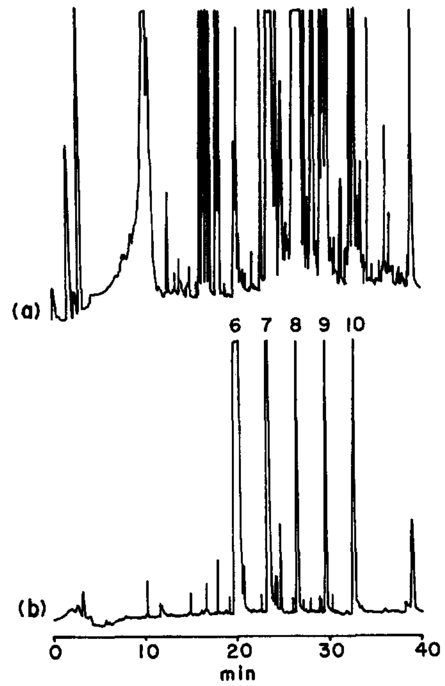


Fig. 6. Chromatograms of (a) Zn(ppb) desorbed thermally at 150°C and (b) n-alcohols ($6–10 = C_6–C_{10}$) retained at 100°C by Zn(ppb) and desorbed via supercritical fluid extraction.

trap containing Cu(dihed) was used for over twenty analyses with no noticeable change in performance.

Another comparison of the difference in blanks between supercritical fluid extraction and thermal desorption can be seen for a sorbent consisting of Zn(ppb) that had undergone repeated heating cycles. The blank obtained by thermal desorption at 150°C (Fig. 6a) was no longer acceptable for use. The chromatogram in Fig. 6b is that of a sample of n-alcohols retained on the sorbent and removed by supercritical fluid extraction. This chromatogram exhibits only a few small peaks that might be attributed to degradation of the sorbent.

We have previously shown that nickel(II) chelates of **I** are effective sorbents for sulfur-containing compounds [17]. Tetrahydrothiophene and di-n-butylsulfide were fully retained by Ni(dihed) at 100°C. Supercritical fluid extraction at 50°C and 80 atm for 10 min completely removed the di-n-butylsulfide, but only removed about half of the tetrahydrothiophene. A subsequent thermal desorption or supercritical fluid extraction led to removal of the remainder of the tetrahydrothiophene. The association between tetrahydrothiophene and nickel(II) complexes with **I** is expected to be greater than that with di-n-butylsulfide because of reduced steric encumbrance in the ring compound [22]. Complete removal of the tetrahydrothiophene in one extraction was accomplished by using a longer extraction time.

Williams and Sievers [20] reported the use of a Eu(III) complex of a 4,4,4-trifluoro-1,3-butanedionyl derivative of Chromosorb 102 as a sorbent for oxygenated compounds in air. We prepared a Cu(II) complex in addition to the Eu(III) complex and investigated the suitability of applying supercritical fluid extraction for removal of retained compounds. With both sorbents we experienced difficulty in obtaining suitable blanks following thermal conditioning or repeated supercritical fluid extraction. The blanks observed after thermal conditioning at 150°C improved for the first 30 min, then notably degraded with further heating. After 45 min at 150°C, the polymers exhibited significant darkening. At temperatures of 100°C, which are necessary for selective retention studies, we were able to obtain a suitable blank (5 min thermal desorption at 100°C) after 30 min of conditioning. The polymer was then subjected to repeated 30-min extractions with supercritical carbon dioxide. The blank (10 min extraction at 50°C and 80 atm) improved after each of the first three extractions, however, the restrictor often clogged during this procedure. Further extractions failed to improve the quality of the blank or eliminate the clogging. Since the blanks were never judged acceptable, no attempt was made to eliminate the clogging of the restrictor, and further study of these sorbents was abandoned.

Seshadri and Kettrup [21] have described the synthesis of a β-ketoamide derivative of silica gel. We prepared the Cu(II) complex of this material but were unable to obtain sufficiently clean blanks at temperatures of 100°C to permit its use as a selective sorbent. Repeated extraction with supercritical carbon dioxide also failed to provide suitably clean blanks at temperatures of 100°C needed for adsorption of donor compounds. Further study of the sorbent properties of this material was therefore abandoned.

CONCLUSIONS

Supercritical fluid extraction with carbon dioxide is an effective means of removing compounds adsorbed on metal polymers with bis β-diketonate ligands. The blanks with supercritical fluid extraction were often better than those obtained using thermal desorption. Pyridine-containing compounds were selectively removed from cigarette smoke using a copper-containing sorbent. Extraction conditions of 200 atm, 100°C and 20 min permitted the complete removal of the pyridine-containing compounds from the sorbent.

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