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Supercritical Fluid Extraction of Toxic Heavy Metals from Solid and Aqueous Matrices

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ABSTRACT

The feasibility of using dithiocarbamate chelating agents or sulfur-containing organophosphorus reagents for the supercritical fluid extraction (SFE) of toxic heavy metals from solid and aqueous matrices was investigated. Effective extraction of heavy metal ions from both sand matrix and water samples was demonstrated by using supercritical CO_2 containing dithiocarbamate chelating agents. A commercially available sulfur-containing organophosphorus reagent, Cyanex 302, was used for the extraction of toxic heavy metals from wood samples. The extraction profiles were initially rapid followed by a very low level of metal extraction, indicating that the process is limited to extraction of leachable toxic metals.

Key Words: Supercritical fluid extraction; Heavy metals; Dithiocarbamate; Organophosphorus reagent.

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INTRODUCTION

Supercritical fluids (SF) are used increasingly as extraction solvents due to increased restrictions on the use of solvents, particularly chlorinated solvents, resulting from environmental legislation. Carbon dioxide (CO_2) has been the solvent of choice due to its low toxicity, relatively low cost, convenient critical properties, and ease of recycling. For extraction of organic compounds, SF CO_2 has been found to be a particularly useful solvent at both analytical and process scales.[1] Direct extraction of metal ions by neat supercritical CO_2 without addition of a ligand is highly inefficient because of the charge neutralization requirement and the weak solute–solvent interaction. However, when metal ions are chelated with organic ligands, they become quite soluble in SF CO_2.[2–6] Conversion of metal ions into metal chelates can be performed by two methods. One method is on-line chelation, which is performed by first dissolving ligands into SF CO_2 then flowing the SF CO_2 through the sample matrix. Another method is in situ chelation, which involves adding the ligands directly to the sample matrix prior to the supercritical fluid extraction (SFE). Both methods have been found to be successful for metal ion extraction using SF CO_2.[2–14]

According to the published research,[2–14] the following factors are important for effective extraction of metal species in supercritical CO_2: (1) solubility of the chelating agent, (2) solubility and stability of the metal chelate, (3) density of supercritical fluids, (4) chemical form of the metal species, and (5) sample matrix. A variety of organic complexing agents have been used in initial studies of SFE of metal ions achieving efficient extraction. It has been observed that the introduction of fluorine-substituted groups to the ligands[2–8,10–13] or using synergistic two-ligand systems[6–8,10–13] can enhance the efficiencies of extraction into supercritical fluids. The method of this enhancement effect is thought to be three-fold: (1) increased solubility of the fluorine-substituted ligands and metal complexes in SF CO_2 over nonfluorine-substituted analogues, (2) increased solubility of metal complexes due to adduct formation, and (3) the capability of the fluorine substituted ligands and synergistic two-ligand systems to extract metal ions from relatively acidic conditions.

The current study focuses on two potential applications of chelation/supercritical fluid extraction: industrial wastewater treatment and environmental remediation. It is well recognized that the presence of heavy metals in the environment can be detrimental to a variety of living species, including humans. A variety of industries are responsible for the release of heavy metals into the environment through their wastewater disposal practices.[15] These industrial sources include the iron and steel production industry, the nonferrous metal industry, mining and mineral processing operations, the pigment manufacturing industry, the wet phosphoric acid process in the fertilizer industry, battery manufacture, the printing and photographic industries, and metal working and finishing processes. This article discusses the SFE of metal ions (including Cd^{2+}, Co^{2+}, Cu^{2+}, Pb^{2+}, Zn^{2+}, As^{3+}, Cr^{3+}, and Cr^{6+}) from spiked solid and liquid matrices and from actual environmental samples using supercritical CO_2 that contains dithiocarbamate chelating agents or organophosphorus reagents. The material presented here lays the groundwork for further research in this area and will, hopefully, accelerate development of industrial-scale metal ion extraction systems.

EXPERIMENTAL

Reagents

The chelating agents, diethylammonium diethyldithiocarbamate (Et_2NH_2DDC), sodium diethyldithiocarbamate (NaDDC), and ammonium pyrrolidinedithiocarbamate (APDC) were purchased from Aldrich (Milwaukee, WI). Lithium bis(trifluoroethyl)dithiocarbamate (LiFDDC) was synthesized according to a procedure outlined in the literature.[16] Bis(2,4,4-trimethylpentyl)monophosphinic acid (Cyanex 302, Cytec) was used as supplied. Liquid carbon dioxide (Air Products, SFE/SFC grade) and methanol (MeOH) modified carbon dioxide (Air Products, SFE/SFC grade) were used as received. Other chemicals used are of ACS grade.

Instrumentation Used

Supercritical CO_2 was supplied via a syringe pump (model 260D, ISCO, Lincoln, NB). The pump head was cooled with a circulating water bath (5°C) to liquefy the gaseous CO_2. The experiments were performed with PEEK extraction cells (9 mL, ISCO, Lincoln, NB) placed in an extractor (SX2-10 ISCO, Lincoln, NB). At the oven exit a silica capillary restrictor (20-cm length, 50-μm i.d.) was used to maintain a constant pressure and supercritical fluid flow though the extraction cell. Inductively coupled plasma mass spectrometry (ICP-MS) (Sciex Elan model 250) was used for analysis of Cd, Co, Cu, Pb, and Zn in the extracted samples.

Procedures

The spiked sand samples were placed in the extraction cell followed by glass wool, with a certain amount of ligand placed above this. The extraction cell was placed into the oven and pressurized with supercritical CO_2 for static extraction followed by opening an exit valve for a dynamic extraction. Variation of extraction time for both the static step and dynamic step was used for various samples. After dynamic extraction, the inlet valve was closed and the cell depressurized slowly via the capillary restrictor. The CO_2 flow rate, as measured by volume of liquid at the pump, was ~1.5 mL/min. The extracts were collected in a small volume of chloroform (~10 mL). When the extraction was completed, the sample matrix was removed from the extraction cell and treated with 20 mL of 1 M nitric acid, which was subsequently analyzed by ICP-MS.

For repeated extractions of wood samples, static time and dynamic periods were utilized. The extraction process was repeated multiple times to determine if all of the extractable metals had been removed. A 50-mg wood sample was used for the SFE experiment. Extracted solutes were trapped in a 30-mL vial with 5-mL methanol. After SFE, the wood sample residue was air dried. Treated and untreated wood samples (10 mg) were analyzed by neutron activation analysis (NAA) for residual heavy metals. The extraction efficiencies were calculated from both the trapped solutions and the wood residues. The data obtained are reported as fraction number where each fraction represents one completed extraction.

NAA was used for the analysis of extracted As, Sb, and Cr samples. The samples were irradiated in a 1-MW Triga nuclear reactor at a steady flux of $6 \times 10^{12}\,\mathrm{N\,cm^{-2}\,s^{-1}}$ for 1 h. After being cooled for several days, the neutron activated samples and standards were counted on an Ortec Ge (Li) detector. The detector has a resolution of 2.3 keV at 1336 keV radiation from ^{60}Co. The amount of metal trapped was determined by calibration of the detector with the standard solution as given previously. The γ-rays of As, Sb, and Cr were emitted at 559, 564, and 320 KeV, with half-lives of 1.10, 2.74, and 27.8 days, respectively.

A specially designed liquid extraction vessel was used for SFE of metal ions from aqueous samples. The liquid extraction vessel was modified from a commercial SFE cell (Dionex, 1.0-cm i.d. and 13-cm length) having a volume of 10 mL. The 1/16-inch stainless steel inlet tubing on the cell was extended to the bottom of the vessel cavity, forcing the supercritical CO_2 to flow through the liquid in the vessel before exiting through the outlet tubing at the top. An aqueous solution containing Cd^{2+}, Co^{2+}, Cu^{2+}, Pb^{2+}, and Zn^{2+} was prepared by spiking a known amount of an atomic absorption standard containing these metal ions into a 0.05 M sodium acetate/acetic acid (NaAC/HAC) buffer solution with a pH of 4.4. In the SFE of the water samples, an excess amount of dithiocarbamate ligand, usually 50 mg, contained in a glass tube plugged with pieces of glass wool at both ends was installed in the supercritical CO_2 inlet line upstream of the liquid extraction vessel. A known volume, usually 5 mL, of a water sample containing divalent heavy metal ions was added to the liquid extraction vessel. SFE was conducted in dynamic mode for 20 minutes. When the extraction was completed, the sample was removed from the extraction vessel and analyzed by ICP-MS.

RESULTS AND DISCUSSION

SFE of Metal Ions from Water Samples Using Dithiocarbamate Chelating Agents

The extraction efficiencies for Cd, Co, Cu, Pb, and Zn from aqueous samples using several dithiocarbamate ligands are shown in Table 1. The results indicate that the fluorinated chelating agent LiFDDC is more effective that its nonfluorinated analogues agents. The extraction efficiency of APDC was the lowest among the four chelating agents. These results indicate that the extraction efficiencies of metal ions from water samples have good correlation with solubilities of related metal chelates in supercritical CO_2. In this case, solubilities of the metal chelates play a key role in extraction efficiencies. The fluorinated metal-dithiocarbamate chelates have higher solubilities in supercritical CO_2 than their nonfluorinated analogues.[6,17]

Table 1. SFE efficiencies of metal ions from water samples.[a]

	Extraction efficiency[b] (%)				
Ligand	Cd	Co	Cu	Pb	Zn
LiFDDC	99	96	95	94	93
$(Et)_2NH_2DDC$	82	82	92	85	74
NaDDC	88	92	90	86	85
APDC	86	90	91	89	88

[a] 2.5 mg/L of each metal ion in aqueous samples buffered by 0.05 M HAC/NaAC to pH 4.4; 20-minute dynamic extraction with supercritical CO_2 at 150 atm and 60°C.

[b] Average data of two runs.

SFE of Metal Ions from Solid Samples

SFE of Transition Metal Ions Using Dithiocarbamate Chelating Agents

Depending on the nature of the matrix, the interactions between solute and matrix may affect the SFE efficiency of the ionic solutes. Sand was used in this study as a solid support. In SFE experiments, 10 μg of each of the following metal ions: Cd^{2+}, Co^{2+}, Cu^{2+}, Pb^{2+}, Zn^{2+}, Cr^{3+}, and Cr^{6+} were spiked on the solid support. This corresponds to about 4.8×10^{-8} moles for Pb^{2+} and about 1.7×10^{-7} moles for Co^{2+}. The amount of LiFDDC used in each experiment was 50 mg, which corresponds to 1.9×10^{-5} moles and is at least an order of magnitude greater than the total amount of metal ions present in the solid samples. Table 2 shows results of the SFE experiments undertaken at 200 atm and 60°C for a 10-minute static extraction followed by a dynamic flushing lasting 15 minutes.

Without the ligand, the extraction efficiencies for the spiked metal ions into neat CO_2 from the solid material are insignificant ($<2\%$). In the presence of LiFDDC, significant amounts of the spiked metal ions can be extracted from the solid material by neat CO_2. The extraction efficiencies of Cd^{2+}, Co^{2+}, Cu^{2+}, Pb^{2+}, and Zn^{2+} were all around 90 to 92% at 200 atm and 60°C. Addition of methanol to the supercritical CO_2 increased the polarity of the fluid phase and enhanced the extraction efficiency for polar solutes. When methanol was added to CO_2 at a 5% concentration (v/v), the extraction efficiencies of these divalent metal ions from sand were further increased to above 95%.

Table 2. Extraction efficiencies of Cd^{2+}, Co^{2+}, Cu^{2+}, Pb^{2+}, Zn^{2+}, Cr^{3+}, and Cr^{6+} from sand by CO_2 and 5% MeOH modified CO_2 at 200 atm and 60°C.[a]

Fluid phase	LiFDDC (mg)	Extraction efficiency[b] (%)						
		Cd	Co	Cu	Pb	Zn	Cr^{3+}	Cr^{6+}
CO_2	0	<2	<1	<2	<1	<1	<1	<2
CO_2	50	92	91	91	90	93	62	70
CO_2 + 5% MeOH	50	97	95	93	97	96	92	94

[a] For Cd,Co, Cu, Pb, and Zn, a 10-μg spiked sample with 10 minutes of static extraction and 15 minutes of dynamic extraction. For Cr^{3+} and Cr^{6+} samples, 10-μg spiked Cr^{3+} or Cr^{6+} sample, 30 minutes of static extraction and 45 minutes of dynamic extraction.

[b] Average data of two runs.

SFE of Cr^{3+} And Cr^{6+} from Solid Materials

In conventional solvent extraction processes, Cr^{3+} in aqueous solution is usually difficult to extract by dithiocarbamate ligands because of the difficulty of displacing the water molecules of coordination from strongly hydrated Cr^{3+} ions. On the other hand, the hexavalent Cr^{6+} species in aqueous solutions can be effectively extracted by dithiocarbamate ligands. This procedure constitutes the basis for chromium speciation as outlined by U.S. EPA methods 218.3 and 218.4.[18] Direct extraction of Cr^{3+} from aqueous phase in solvent extraction is difficult because of strong solvation of water with Cr^{3+}, which prohibits its chelation with FDDC in aqueous/organic solvent extraction. One alternative is to first oxidize Cr^{3+} to Cr^{6+} by adding potassium permanganate ($KMnO_4$) and the resulting solution can then be processed by solvent extraction with dithiocarbamate ligands. The difference in the amount of Cr^{6+} before and after oxidation can be used to determine the amount of Cr^{3+}in aqueous solution. Direct extraction of chromium species from solid samples by SFE has not been reported in the literature. The feasibility of extracting the chromium species from solid materials by supercritical CO_2 was evaluated in a series of experiments where known amounts (10 μg) of Cr^{3+} and Cr^{6+} were spiked (separately) onto 300 mg of sand. The solid samples before and after the extraction were analyzed by a nondestructive NAA technique. The metal chelates extracted from the sample and collected in chloroform were also determined by the nondestructive NAA and the results are summarized in Table 2. An interesting observation in this SFE study is that Cr^{3+} can be extracted from sand by supercritical CO_2 containing LiFDDC at conditions of 60°C and 200 atm with extraction efficiencies approximately 62%. Supercritical CO_2 amended with methanol and containing LiFDDC can extract spiked Cr^{3+} with a extraction efficiency up to 92% from the sand matrix. This mechanism is not clear. The extraction efficiencies of Cr^{6+} by supercritical CO_2 containing LiFDDC were slightly higher than those observed for Cr^{3+} under the same conditions. These results are different from the known behavior of aqueous Cr^{3+} in conventional solvent extraction. The strong solvation of water by Cr^{3+}, which prohibits chelation of the trivalent species by LiFDDC in conventional solvent extraction, is not a problem in SFE of Cr^{3+} spiked on solid materials. Since both Cr^{3+} and Cr^{6+} species can be simultaneously and effectively extracted by supercritical CO_2/methanol/LiFDDC, this in situ chelation-SFE method can be used for the determination of total extractable chromium from solid samples directly. Experimental results also indicated that with the same extraction scheme, 300 mg of Cyanex 302 can also quantitatively extract both chromium species (data not shown).

SFE of CCA in Wood Sample Using Organophosphorus Reagent—Cyanex 302

The most commonly available treated wood is impregnated with chromated copper arsenate (CCA). It is used for the long-term protection of wood against attack by fungi and insects. Applying such wood preservatives extends the product life and helps reduce the demand for forest resources. CCA-treated wood is used primarily for outdoor settings, such as construction of decks, utility/telephone poles, picnic tables, and so forth. However, with time, small amounts of chromium, copper, and arsenic will leach out to the surrounding soil. For outdoor playground equipment, CCA can be leached into the ground and children can be exposed to the contaminants. Concerns about environmental contamination by heavy metals have led the U.S. EPA to review the registration of CCA and the Consumer Product Safety Commission is considering a petition from environmental groups seeking a ban on the use of CCA-treated wood in playground structures. The U.S. EPA has reached a voluntary agreement with industry to phase out the use of CCA for treating wood for residential structures by December 31, 2003.[19]

SFE was tested for removal of CCA from wood samples. The concentration of CCA in treated wood varies depending on the specific purpose of the lumber and manufacturer formulation of the CCA solution. The concentrations of Cr, Cu, and As in a wood sample from a telephone pole were measured to be 18223, 9425, and 20054 μg/g, respectively by NAA. A 50-mg sample of this telephone pole wood was dried and ground and then subjected to repeated batchwise extractions. Extractions took place at a pressure of 200 atm and 60°C using supercritical CO_2 with 5% MeOH and 1 g of Cyanex 302 ligand for each extraction. Each batch extraction process was carried out for 10-minute static extraction followed by 30-minute dynamic extraction. Results are shown in Fig. 1. A high extraction efficiency was observed for the first three extractions, followed by a much lower extraction rate for subsequent extractions. The first batch showed the highest extraction efficiency and the amount of Cu, As, and Cr extracted are 3500, 900, and 340 μg/g, respectively. After seven consecutive batchwise extractions, the cumulative Cu, As, and Cr extracted were approximately 7500 μg/g, 4000 μg/g, and 1300 μg/g, respectively. Significant quantities of Cu can be removed from the wood samples. The extraction efficiency is most favorable in the order of $Cu \gg As > Cr$. After the seven batch extractions, the extraction profile showed diminishing recoveries, indicating that a fraction of the metal species in the wood cannot be extracted under these experimental conditions. The active sites and natural ligands presented in the wood samples may bind strongly to certain metal ions, thereby only a relatively small amount of metals are

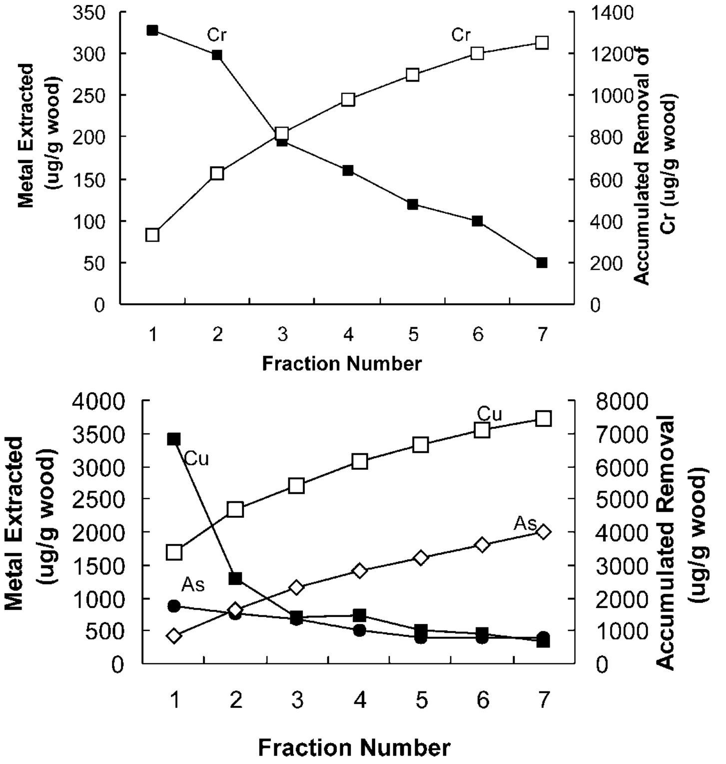

Figure 1. Extraction of heavy metals (including As, Cr, Cu) from a CCA-treated wood sample. Sample was extracted at 60°C and 200 atm using supercritical CO_2 containing 5% MeOH. Each batch extraction was carried out for 10-minute static extraction and 30-minute dynamic extraction.

leachable. Using SFE technology to remove leachable metals from the CCA-treated wood can significantly reduce the risk of such materials leaching metals into the environment.

CONCLUSION

Metal ions including Cd^{2+}, Co^{2+}, Cu^{2+}, Pb^{2+}, Zn^{2+}, Cr^{3+}, and Cr^{6+} can be effectively removed from solid matrices, such as sand and aqueous solutions, by supercritical CO_2 containing dithiocarbamate ligands. The results suggest that the solubilities of the metal chelates in the supercritical fluid play a key role in determining the efficiencies of SFE of metal ions from aqueous phase and relatively inert solid matrix. Fluorination of the chelating agent (as in the case of LiFDDC) increases the solubilities of the metal chelates and subsequently enhances the extraction efficiencies of the metal ions. It is demonstrated that a leachable fraction of metals in real environmental samples (CCA-treated wood) can be extracted by Cyanex 302 in supercritical CO_2, reducing the risk of such materials leaching toxic metals into the environment.

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REFERENCES

1. Hawthorne, S.B. Analytical-scale supercritical fluid extraction. Anal. Chem. **1990**, *62*, 633A.
2. Laintz, K.E.; Wai, C.M.; Yonker, C.R.; Smith, R.D. Solubility of fluorinated metal diethyldithiocarbamate in supercritical carbon dioxide. J. Supercrit. Fluids **1991**, *4*, 194–198.
3. Laintz, K.E.; Wai, C.M.; Yonker, C.R.; Smith, R.D. Extraction of metal ions from liquid and solid materials by supercritical carbon dioxide. Anal. Chem. **1992**, *22*, 2875–2878.
4. Lin, Y.; Brauer, R.D.; Laintz, K.E.; Wai, C.M. Supercritical fluid extraction of lanthanides and actinides from solid materials with a fluorinated β-diketone. Anal. Chem. **1993**, *65*, 2549–2551.
5. Wai, C.M.; Lin, Y.; Brauer, R.D.; Wang, S.; Beckert, W.F. Supercritical fluid extraction of organic and inorganic mercury from solid materials. Talanta **1993**, *40*, 1325–1330.
6. Lin, Y.; Smart, N.G.; Wai, C.M. Supercritical fluid extraction and chromatography of metal chelates and organometallic compounds. Trends Anal. Chem. **1995**, *14* (3), 123–133.
7. Lin, Y.; Wai, C.M.; Jean, F.M.; Brauer, R.D. Supercritical fluid extraction of thorium and uranium ions from solid and liquid materials

with fluorinated β-diketones and tributyl phosphate. Environ. Sci. Technol. **1994**, *28*, 1190–1193.

8. Lin, Y.; Wai, C.M. Supercritical fluid extraction of lanthanides with fluorinated β-diketones and tributyl phosphate. Anal. Chem. **1994**, *66*, 1971–1975.
9. Lin, Y.; Smart, N.G.; Wai, C.M. Supercritical fluid extraction of uranium and thorium from nitric acid solutions with organophosphorus reagents. Environ. Sci. Technol. **1995**, *29*, 2706–2711.
10. Wai, C.M.; Lin, Y.; Ji, M.; Toews, K.L.; Smart, N.G. Extraction and separation of uranium and lanthanides with supercritical fluids. In *Metal Ion Separation and Preconcentration: Progress and Opportunities*; Bond, A.H., Dietz, M.L., Eds.; ACS Symposium Series 716; American Chemical Society: Washington, DC, 1999; 390–400.
11. Lin, Y.; Wu, H.; Smart, N.G.; Wai, C.M. Investigation of adducts of lanthanide and uranium β-diketonates with organophosphorus lewis bases by supercritical fluid chromatography. J. Chromatogr. A **1998**, *793*, 107–113.
12. Lin, Y.; Wu, H.; Smart, N.G.; Wai, C.M. Separation of divalent transition metal β-diketonates and their adducts by supercritical fluid chromatography. Talanta **2000**, *52*, 695–701.
13. Lin, Y.; Wu, H.; Smart, N.G.; Wai, C.M. System optimization of in-situ chelation/supercritical fluid extraction of lanthanides and actinides using a radiotracer technique. Sep. Sci. Technol. **2001**, *36*, 1149–1162.
14. Elshani, S.; Smart, N.G.; Lin, Y.; Wai, C.M. Application of supercritical fluids to the reactive extraction and analysis of toxic heavy metals from environmental matrices. Sep. Sci. Technol. **2001**, *36*, 1197–1210.
15. Williams, C.J.; Aderhold, D.; Edyvean, R.G.J. Comparison between biosorbents for the removal of metal ions from aqueous solutions. Water Res. **1998**, *32*, 216–224.
16. Sucre, L.; Jennings, W. Lithium di(trifluoroethyl)dithiocarbamate: an alternative reagent for the preparation of di(trifluoroethyl)dithiocarbamate metal-chelates. Anal. Lett. **1980**, *13*, 497.
17. Wai, C.M.; Wang, S.; Liu, Y.; Lopez-Avila, V.; Beckert, W.F. Solubility parameter and solubility of metal dithiocarbamates in supercritical carbon dioxide. Talanta **1996**, *43*, 2083–2091.
18. U.S. EPA, Methods for Chemical Analysis of Waters and Wastes, Cincinnati, Ohio, **1983**.
19. Chemical & Engineering News, Feb. 11, **2000**, p. 9.

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