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Elution of Gold from Activated Carbon Using Supercritical Carbon Dioxide

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ABSTRACT

A novel method for the desorption of gold from activated charcoal is reported. Ion pair solvation of sodium dicyanoaurate (I) ($Na^+ \ldots Au(CN)_2^-$) by tributylphosphate facilitates the charge neutralization necessary for the elution of the ionic $Au(CN)_2^-$ by the non-polar supercritical carbon dioxide. The method is sensitive to pressure and temperature, and the static (no CO_2 flow) period is more significant than the dynamic (CO_2 flow) period. The presence of water is necessary to effect extraction.

INTRODUCTION

Supercritical fluids have generally been used for the extraction of nonpolar organic compounds. In those instances where polar organic compounds have been extracted, it was necessary to increase the polarity of the fluid in order to achieve the concept of "like dissolves like." A few reports on the use of supercritical carbon dioxide ($SC\text{-}CO_2$) for the extraction of metal ions and other inorganic complexes have appeared in the literature (e.g., 1–6).

The challenge in extracting metal ions by nonpolar carbon dioxide arises from the large loss in electrostatic energy that will accompany the process (7, 8). A necessary condition for the extraction of metal ions (or ionic species in general) is a lowering of the electrostatic energy of the process by neutralization of the ion's charge. This can and has been accomplished

by modifying the CO_2 with chelating (complexing) agents or by spiking the sample matrix with chelating agents and leaching the complexes formed with SC-CO_2 (e.g., 1–6). Such methods have been used to accomplish the extraction of, for example, some lanthanides, Th, U, Hg, Zn, and Cu. The ligands used include tributylphosphate, β-diketones, and crown ethers.

The use of activated charcoal for the extraction of gold from cyanide leach solutions was realized in 1894 (9) and is widely used in the carbon-in-pulp, carbon-in-leach, and carbon-in-column processes. The recovery of the adsorbed gold from activated charcoal was revolutionized by the work of Zadra and coworkers (10) in 1952. Their method involves soaking the gold-laden carbon in a solution containing approximately 1% w/v NaOH and 0.1% w/v NaCN at 90°C for upward of 24 hours, and electrowinning to recover the desorbed gold. Various modifications of this method have also been reported. Reports have also appeared in the literature where gold was eluted from activated carbon using solutions containing organic solvents (for example, ethanol, acetone, and acetonitrile) with or without cyanide present (11–15).

Gold is adsorbed on carbon as the dicyanoaurate(I) complex ion, $Au(CN)_2^-$, from a NaCN solution. The dicyanoaurate(I) ion is not expected to dissolve in the nonpolar CO_2. However, charge neutralization by a cation to form an ion paired species will facilitate its dissolution. Although the mechanism of gold adsorption on activated charcoal was in contention for some time, the proposal of ion pairing $[M^{n+} \ldots (Au(CN)_2^-)_n]$ seems to be favored (16, 17). Solvation extraction of $M^{n+} \ldots (Au(CN)_2^-)_n$ ion pairs with various neutral organophosphates and amines has also been reported (18, 19).

A novel method of eluting gold from activated carbon using SC-CO_2 is described in this paper. This author is not aware of any earlier report(s) on the use of supercritical CO_2 to elute $Au(CN)_2^-$ from activated charcoal.

EXPERIMENTAL SECTION

Materials

Activated charcoal (Type GRC-11 12 × 30) was obtained from Calgon Carbon Corporation (Pittsburgh, PA). Gold standard solutions in deionized water were made from $KAu(CN)_2$ obtained from Johnson Matthey (Ward Hill, MA). The solution from which gold was adsorbed on the carbon also contained 250 mg/L NaCN. NaCN of reagent-grade quality was obtained from Sigma Chemical Co. (St. Louis, MO).

The activated charcoal was washed to remove fines and dried overnight in an oven at 100°C. A weighed amount (40 g) was contacted with 200 mL

of 100 mg/L gold solution for 7 days in a beaker which was opened and stirred at least twice a day. The carbon was separated from the solution by suction filtration (through a Whatman No. 4 filter paper) and transferred to a tight-capped plastic bottle. The extent of gold loading of the carbon (which was 0.5 mg/g) was calculated from the difference in the concentration of gold in solution before and after the loading (contact) period. The water content of the loaded carbon was determined from the difference in the weights of wet samples and after drying in the oven until constant weight was obtained.

SFE/SFC grade SC-CO_2 (with a helium head pressure of 2000 psi) was obtained from Air Products and Chemicals, Inc. (Allentown, PA). Extraction pressures were achieved with a Spe-ed SFE pump from Applied Separations (Allentown, PA).

Procedure

One gram of the loaded activated charcoal was placed in a 2.5-mL Keystone (Bellefonte, PA) extraction vessel. The vessel was connected online in a modified GOW-MAC Model 69-750 gas chromatograph oven, and 10 minutes was allowed to preheat the vessel to the desired temperature before pressurizing with CO_2 in the static (no SC-CO_2 flow) mode. It should be noted that the temperature equilibration (preheating) time was chosen arbitrarily, so it is possible that it was insufficient time for the whole extraction vessel to have attained temperature equilibrium. Depressurization during the dynamic (SC-CO_2 flow) mode was achieved with a 75-μm i.d. (12″ long) fused silica tube (Polymicro Technologies, Inc., Tucson, AZ) which was enclosed in a homemade heated aluminum block. The sample collection vessel containing 5 mL of methanol was also placed in a homemade heated nest. Duplicate extractions were performed.

A schematic diagram of the extraction system is shown as Fig. 1. Valve A was a Hewlett-Packard micro-check valve for added prevention against backflow into the tank. Valve B was a Whitey SS3HNBS4 on/off valve (rated 10,000 psi) to enable putting on and taking off the extraction vessel without loss of CO_2. Valve C (Whitey 3NBS4-G; rated 6000 psi) was used to control the dynamic/static (SC-CO_2 flow/no flow) regimes of the extractions. The depressurized carbon dioxide was vented into the fume hood through a 350-μm i.d. fused silica tube that was threaded into a flexible duct.

Gold was determined by atomic absorption spectrophotometry on a Perkin-Elmer Model 107 AA using an acetylene/air flame. The extracts did not need any further treatment, except dilution.

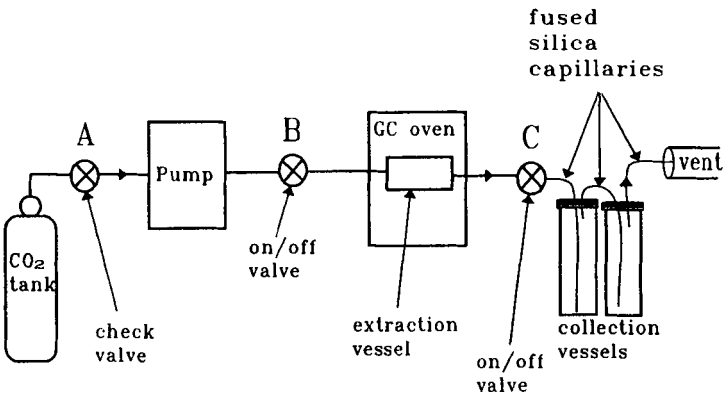

FIG. 1 Schematic diagram of the extraction system. Component functions are described in the text.

RESULTS AND DISCUSSION

Other methods (mentioned above) of desorbing gold from activated carbon have shown that temperature is the most important parameter (11–15, 20). Also, the presence of NaCN is crucial for the desorption of gold both by the Zadra procedure and the procedures that employ a caustic/cyanide solution containing an organic solvent (12, 21). Therefore, 1 mL of 1 M NaCN was added to 1 g of the wet gold-loaded carbon and extracted at the temperatures shown in Table 1. The average water content of the wet

TABLE 1
Effect of Temperature on the Elution of Gold from Activated Carbon with SC-CO_2[a]

Temperature (°C)	% Gold extracted	
50	1.4	
100	6.4	30.9[b]
150	27.2	73.4[b]

[a] Conditions: 4000 psi; 1 g wet gold-loaded activated charcoal; 1.0 mL of 1 M NaCN; static time = 30 minutes and dynamic time = 20 minutes.

[b] Contained 1 mL TBP and 0.5 mL 1 M NaCN, 6000 psi.

TABLE 2
Effect of Static and Dynamic Regime Times on the Elution of Gold[a]

Static time[b] (minutes)	% Au extracted	Dynamic time[c] (minutes)	% Au extracted
0[d]	17.4	10	26.8
30	32.1	15	29.4
60	38.6	20	32.1
180	61.1		

[a] Conditions: Temperature = 150°C; 6000 psi; 1 g wet activated carbon + 1.5 mL of 1 M NaCN.
[b] Dynamic time = 20 minutes.
[c] Static time = 30 minutes.
[d] Vessel allowed 10 minutes to attain temperature equilibrium (as indicated in text).

carbon was 30 ± 4%. It is apparent that a high temperature, 150°C, was also necessary to achieve higher recovery of gold with SC-CO_2 elution.

Previous liquid–liquid extraction work by Miller and co-workers (19, 21) has shown that organophosphorus esters can solvate and quantitatively extract $M^+ \ldots Au(CN)_2^-$ ion-pairs [to form $NaAu(CN)_2.p$TBP, where p is the number of TBP molecules solvating the ion pair. Mooiman and Miller reported that p changes with the concentration of TBP (19)]. The presence of NaCN was necessary for TBP solvation extraction. The ion-pair–TBP solvate adduct is more hydrophobic than the ion-pair itself. It is therefore conceivable why the elution of gold from activated carbon by nonpolar supercritical CO_2 should be favored by the presence of TBP as shown in Table 1, where 27% gold was extracted in the absence of TBP but 73% was extracted in the presence of TBP.

TABLE 3
Effect of SC-CO_2 Pressure on the Elution of Gold from Activated Carbon at 150°C[a]

Pressure (psi)	% Gold extracted
2000	11.6
4000	27.2
6000	32.1

[a] Conditions: Temperature = 150°C; 1 g wet activated carbon + 1.5 mL of 1 M NaCN; static time = 30 minutes and dynamic time = 20 minutes.

TABLE 4
Effect of Ionic Strength on the Elution of Gold from Activated Carbon by SC-CO_2[a]

Condition	% Gold extracted
Dry charcoal	0.3
Dry charcoal + 1.5 mL H_2O	2.9
Dry charcoal + 1.5 mL 1 M NaCN	32.1

[a] Conditions: 6000 psi; temperature = 150°C; static time = 30 minutes and dynamic time = 20 minutes.

In order to test the recovery of gold by the SC-CO_2 process, standard gold solutions were placed in the vessel and extracted in the presence and absence of TBP. A comparison of AA results with those standards that were not subjected to the extraction procedure revealed quantitative recovery.

In order to optimize the SC-CO_2 elution of gold from carbon, it was necessary to examine how the static and dynamic time periods affected the process. The results shown in Table 2 indicate that the static time regime is more important than the dynamic time segment of the process. The small increase in percent gold eluted when the dynamic time was varied (with a static period constant of 30 minutes) was not indicative that some dramatic change would happen, so extending the dynamic time beyond 20 minutes was not viewed as necessary. Table 3 shows that the SC-CO_2 pressure has a significant influence on the percent gold eluted.

Some proponents of the use of organic solvent solutions to desorb gold from activated carbon contend that the presence of NaCN is not necessary (11, 12, 14). In the present instance of using SC-CO_2, suppose time is not a constraining factor (of course, it is) in the sense that we want to eliminate the addition of TBP. As shown in Table 2, a static time greater than 3 hours could lead to quantitative desorption of gold. The question was asked: Is the presence of NaCN necessary to achieve desorption? A gold-loaded carbon sample was dried overnight in an oven at 100°C and desorbed under the conditions shown for Table 4. It is certainly apparent that the presence of NaCN is necessary. Miller et al. (21) reported that 0.3 M NaCN was the minimal concentration necessary to achieve quantitative solvation extraction of $Na^+...Au(CN)_2^-$ ion-pairs by TBP.

CONCLUSION

This is one of the few instances where an inorganic anionic species has been mobilized into SC-CO_2. NaCN is the largest waste in the hydrometal-

lurgy of gold. The use of supercritical CO_2 in the desorption step, where a high concentration of NaCN is currently needed, will drastically reduce the amount of NaCN required (for example, 0.1% w/v in the Zadra method). In the present SC-CO_2 method the requisite amount of NaCN to maintain the ion-pair will already be available from the wet loaded activated carbon (which contained 250 mg/L NaCN and the loaded carbon was 30% wet, i.e., ca. 0.001% w/v NaCN).

An electrochemical process to recover the eluted gold from the methanol collection solution is being studied. An additional advantage offered by this method is that the CO_2 can be recompressed and recycled. In the meantime, a reduction in the cost of CO_2 is being sought through the use of a cooling unit that precedes the pump, whereupon the less expensive regular CO_2 can be used. There is also recent evidence pointing to lower solubility in SC-CO_2 with a helium head (22, 23). An intergrated adsorption/desorption unit is currently under construction.

La Brooy et al. (24) reported an extensive list of organic mining reagents (used as frothers, flotation collectors, grinding agents, etc.) that will inevitably be present in the liquor from which gold is to be recovered. They found that some of these organic compounds affected activated carbon performance in the gold adsorption circuit. It will be of interest to evaluate these organics' ability to aid the desorption of gold with SC-CO_2 as TBP did, or otherwise.

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