

Carrying Gold in Supercritical CO₂

Jeremy D Glennon, Stephen J Harris, Andrew Walker, Conor C McSweeney and Mark O'Connell

Analytical Division, Department of Chemistry, University College Cork, Ireland,
Email: j.glennon@ucc.ie

Received: 23 March 1999

A series of fluorinated calixarene derivatives, with lower rim sulfur-donor atoms, were synthesized and studied for the sequestration of gold using supercritical fluid extraction. Following temperature and pressure optimization and using extracts collected in methyl *iso*-butyl ketone, analysis by flame atomic absorption spectrometry reveals that Au(III) can be efficiently complexed and extracted by a novel calix[4]arene thiourea reagent in supercritical CO₂.

INTRODUCTION TO SUPERCRITICAL FLUIDS

Supercritical fluids, especially those based on inert substances, are considered as 'clean' solvents, free from the environmental concerns of disposal, handling and toxicity associated with organic solvents. A pure supercritical fluid is a substance above its critical temperature and pressure (1). Above its critical temperature, it does not condense or evaporate to form a liquid or a gas but is a fluid with properties changing continuously from gas-like to liquid-like as the pressure increases. Above the critical temperature T_c and pressure P_c , increasing the pressure increases the density and thus the solvating power of the fluid. *It is this solvating power that makes supercritical fluids useful in such processes as the decaffeination of coffee and in the extraction of many important industrial chemicals including medicinal compounds, natural oils and flavours and even, organic pollutants.*

The critical parameters for just three of the many important substances useful as supercritical fluids are given in Table 1. Supercritical fluids can replace liquid solvents in many processes such as extractions from solids, counter-current multistage separations, chromatographic separations and chemical reactions.

Table 1 Critical Parameters for Selected Supercritical Fluids

	$T_c(^{\circ}\text{C})$	$P_c(\text{atm})$
CO ₂	31.3	72.9
N ₂ O	36.5	72.5
H ₂ O	374.1	217.7

In reacting systems, supercritical fluids can make possible homogeneous reactions by dissolving reactants, influence reaction equilibria and rates, and open up the way for new syntheses. In materials science, solid materials can be processed into very uniform fine particles and thin film production, material coating, impregnation and dyeing have recently been demonstrated (2).

One compound, CO₂, has so far been the most widely used for supercritical fluid extraction (SFE) because of its convenient critical temperature, cheapness, non-explosive character and non-toxicity. While generally applicable to the extraction of non-polar organic compounds, the addition of small amounts of modifiers such as the lower alcohols, extends the use of supercritical CO₂ (SF-CO₂) to many polar compounds. Highly valuable extracts from medicinal plants have been obtained using SF-CO₂ for extraction and it is the solvent of choice in many applications including

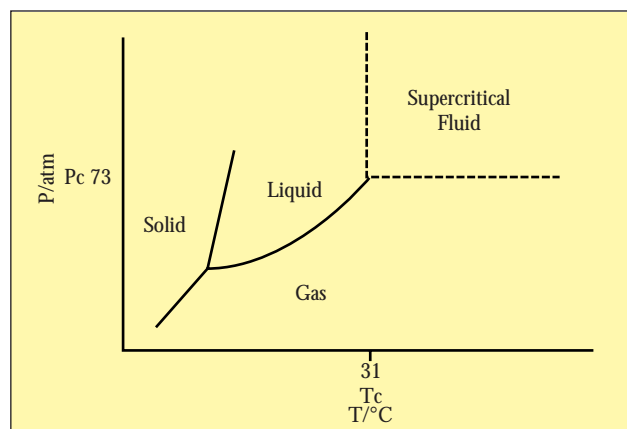


Figure 1 Phase diagram for carbon dioxide

supercritical fluid chromatography. In addition, it has several advantages as an enzymatic reaction medium over conventional organic solvents, which include gas-like diffusivities and liquid-like densities. There is also at present, considerable interest in the fascinating properties of subcritical and supercritical water as solvent and reaction media.

METAL COMPLEXES IN SUPERCRITICAL CO₂

Surprisingly, the first demonstration of the solvating power of supercritical fluids involved metal species *ie* cobalt and iron chlorides in supercritical ethanol in 1879. However, since then the emphasis has been on the extraction of organic compounds, with recently a revival in interest in metal extraction. As in organic solvents, free metal ions are insoluble in supercritical CO₂ because of the charge neutralization requirement and the weak solute-solvent interactions. However, when metal ions are bound to well chosen organic complexing reagents or ligands, they can become quite soluble in supercritical CO₂. Such reagents, depending on chemical structure, can complex metal ions in a polydentate or macrocyclic manner.

Metal complexes have been separated and extracted using SF-CO₂. Wenclawiak *et al* have described the chromatographic separation of cobalt and chromium acetylacetonate complexes using CO₂ modified with methanol (3). In other work, a mixture of ferrocenes was shown to dissolve in pure supercritical CO₂ (4). A fluorinated diketone, namely 2,2,-dimethyl-6,6,7,7,8,8,8-heptafluoro-3,5-octanedione has also been employed to remove lanthanides and actinides from solid materials (5). More recently, Wai has demonstrated that Cu(II) and Hg(II) can be extracted from solid matrices by supercritical CO₂ containing lithium bis(trifluoroethyl)dithiocarbamate (LiFDDC). The choice of the fluorinated ligand is based on the fact that the solubilities of the fluorinated metal complexes are several orders of magnitude higher than the non-fluorinated analogues (6).

OXIDATION STATES AND COMPLEXATION OF GOLD

Precious metals such as gold and silver, in their normal oxidation states (gold in I and III and silver in I), tend

to form their most stable complexes with ligands containing 'soft' donor atoms (7). Thus complexing reagents with N- and especially S-donor atoms form strong complexes with the precious metals. In particular, Au(I) forms its most stable compounds when bonded to 'soft' ligands, containing sulfur or phosphorus and is stabilized with respect to disproportionation by such complexation (8). As medicinal compounds, gold(I) thiolates (AuSR)_n have been studied in relation to chemotherapy for rheumatoid arthritis. Au(III) is invariably complexed in all solutions, usually as anionic species such as [AuCl₄]⁻ and can be solvent-extracted by ion pairing with an oxonium ion from dilute HCl solutions into ethyl acetate and diethyl ether with a very high partition coefficient (9).

Gold metal is chemically unreactive and is not attacked by oxygen or sulfur, but reacts readily with halogens or with solutions containing or generating chlorine such as *aqua regia*; it also dissolves in cyanide solutions in the presence of air or hydrogen peroxide to form [Au(CN)₂]⁻. The reduction of solutions of AlCl₄⁻ by various reducing agents may, under suitable conditions, give highly coloured solutions containing colloidal gold. The complexation of gold for the purpose of extraction from ores has mainly been carried out using cyanide as reagent (10). The most important method for extracting gold is by treating finely crushed ore with sodium cyanide in the presence of oxygen to give a sodium gold cyanide complex, which is typically adsorbed onto activated carbon, before being re-extracted and reduced to the metal (11). Major problems with the cyanidation process are the relatively slow dissolution kinetics and the health and environmental problems associated with it. Generally, alternative gold complexing reagents while less toxic, are less robust, excessively consumed and less economically viable. Complexation has also been shown to play a role in controlling the oxidative power of Fe(III), used in acidic solution as an oxidant for Au(0) (12). In a patent specification Kenna suggested that complexation of the ferric ions could be utilized in reducing their oxidative power to a level where oxidation of gold still proceeded at an acceptable rate, while the oxidation of thiourea was greatly reduced (13). In a separate patent, Nagaraj found that when alkyl hydroxamic acids or their salts were used alone or in conjunction with traditional sulfide collectors on sulfide ores, the kinetics of flotation and overall recovery of the precious metals had increased significantly (14).

Precious metals usually exist together with a large

excess of 'base metals', such as copper and iron. With the growing emphasis on economically feasible recycling and recovery processes, there are increasing demands for highly selective separation techniques and reagents for the separation and recovery of precious metals from low quality ores and secondary sources. High selectivity can be provided by macrocyclic extractants.

SELECTIVE MACROCYCLIC EXTRACTANTS FOR GOLD

A vast array of experimental data available demonstrates that the most effective Au(III) sorbents and extractants from HCl solutions should be found among the compounds containing atoms of ether and oxide oxygen as reaction centres (15). On going from linear polyethers to their macrocyclic analogues, crown ethers have been shown to be the most promising class of extractants for selective gold recovery from chloride solutions. The size of the macrocyclic cavity essentially influences the gold extraction. Derivatives of 18-crown-6 were used by Yakshin and coworkers (15) in the extraction of trace quantities of gold from HCl, while Fang and Fu (16) used benzo-15-crown-5 in the presence of potassium chloride to extract Au(III). Trom *et al* (17) studied the solvent extraction and transfer through bulk liquid membranes of gold and silver cyanide complexes using dicyclohexano-18-crown-6. The same group investigated the solvent extraction and transport through a supported liquid membrane of metal cyanide complex salts of gold (I) and silver (I) by macrocyclic extractant carriers (18). Bradshaw *et al* have developed silica gel bonded thiamacrocycles which have shown high selectivity for Au(III) (19).

GOLD EXTRACTION USING SUPERCRITICAL FLUIDS

Reports of gold extraction by SFE are few and far between but what is in the literature is interesting. Wai *et al* have reported the extraction of Au(III) from cellulose paper using bistriazolo-crowns in supercritical CO₂ (20). In the presence of 5% methanol as a modifier and the addition of microlitre quantities of water, up to 80% of the spiked gold was extracted. In the absence of the modifier and spiked water, the extraction efficiency was insignificant. Otu recently

reported the desorption of gold from activated carbon using supercritical carbon dioxide (21). Ion pair solvation of sodium dicyanoaurate by tributyl phosphate facilitates the charge neutralization necessary for the elution of the ionic Au(CN)₂⁻ by the non-polar supercritical carbon dioxide.

The objective of this research into supercritical fluid extraction is to avoid the use of organic modifiers and to maximize the extraction selectivity for gold. The key here is the matching of the gold coordination chemistry with a SF-CO₂ soluble ligand, such as through the careful choice of donor atoms in a macrocyclic cavity. In the work reported in this paper, the use of new fluorinated macrocyclic reagents (Figure 2), based on the aptly named calixarene 'molecular baskets' is described. The SFE of Au(III) from spiked cellulose-based filter paper is chosen as a convenient approach to test the efficiencies of the new reagents.

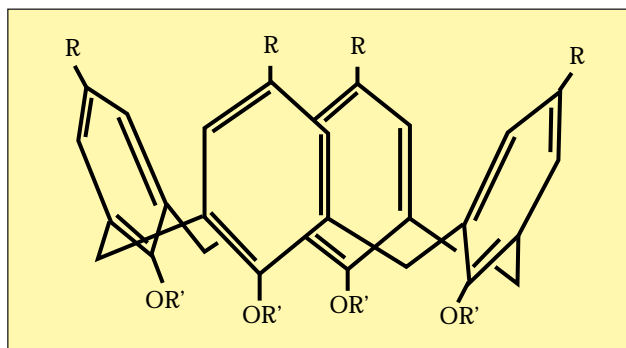


Figure 2 Chemical structures of the fluorinated calixarenes studied for the SFE of gold

- C1:** $R = -(CH_2)_3S(CH_2)_2(CF_2)_7CF_3$;
 $R' = -CH_2(C=O)NHOH$
- C2:** $R = -(CH_2)_3S(CH_2)_2(CF_2)_7CF_3$;
 $R' = -CH_2(C=S)N(C_2H_5)_2$
- C3:** $R = -(CH_2)_3S(CH_2)_2(CF_2)_7CF_3$;
 $R' = -CH_2(C=O)N(CH_2CH_2SH)(CHCH_3CH_2CH_3)$
- C4:** $R = tert\text{-}butyl-$;
 $R' = CH_2(C=O)O(CH_2)_2NH-$
 $(C=S)NH(CH_2)_3S(CH_2)_2(CF_2)_7CF_3$

EXPERIMENTAL

Materials

A 1000 ppm Spectrosol standard solution of Au(III) as AuCl₄⁻ was obtained from Merck (Germany). Hydroxylammonium chloride (NH₂OH.HCl) was also bought from Merck. All CO₂ gas cylinders were fitted with dip tubes and bought from Irish Oxygen (Cork, Ireland). All extracted samples after SFE were collected in either methyl iso-butyl ketone (MIBK) or DMSO (both purchased from Merck) as indicated.

Synthesis of Fluorinated Calix[4]arene Reagents

The chemical structures of three sulfur-containing fluorinated calixarenes are given in Figure 2, alongside the tetra-hydroxamate (C1). The synthesis of upper rim allyl calixarenes, for subsequent thiolene addition reaction to yield fluorinated derivatives, has been reported elsewhere by members of this laboratory (22). Synthetic methods for lower rim functionalization, to provide donor atoms for selective metal ion complexation, such as for Fe(III) with hydroxamate (C1) and for Ag(I) with thioamide groups (C2), are now also well established. As the emphasis in this work is on the application of these macrocyclic reagents for gold extraction, only the synthesis of the novel lower rim fluorinated derivative and the most effective reagent (C4) is given below.

Synthesis of p-t-butylcalix[4]arenetetra-1-heptadecafluorodecylthio-n-propyl-3-(2-ethyl)-2-thiourea acetate (C4)

To 0.8 g (0.005 moles) HOCH₂CH₂NH(C=S)NHCH₂CH=CH₂ (Aldrich) was added 2.4 g (0.005 moles) heptadecafluorodecanethiol (22) in 6.0 g 1,2-dichloroethane and 200 mg AIBN. The entire mixture was refluxed under nitrogen for 2 h following which a further 200 mg of azoisobutyronitrile was added and a further 2 h period of reflux was carried out. After cooling, all volatiles were removed to give a buff-coloured waxy solid of HOCH₂CH₂NH(C=S)NH(CH₂)₃S(CH₂)₂(CF₂)₇CF₃ (3.15 g, 98% yield). ¹H-NMR spectral analysis verified the absence of a chemical shift resonance at 5.92m for =CH from the allyl functionality of the reactant.

To 0.55 g (0.000625 mole) p-*tert*-butylcalix[4]arene tetraacetic acid was added 5 ml thionyl chloride and the entire mixture was refluxed, with stirring, for 2 h (calcium chloride tube attached during reaction period). After this period, all the volatiles were removed under reduced pressure to give the corresponding p-*tert*-butylcalix[4]arene tetra-acid chloride. To this solid was added 10 ml dry THF, followed by 0.198 g (0.0025 mole) dry pyridine and 1.6 g (0.0025 mole) HOCH₂CH₂NH(C=S)NH(CH₂)₃S(CH₂)₂(CF₂)₇CF₃ in 5 ml dry THF and the entire mixture was stirred at room temperature overnight under nitrogen. Following this time, all volatiles were removed and the residual pale yellow solid was washed with 5% aqueous HCl and then water. The resulting sample was allowed to air dry overnight to afford 2.0 g of the crude product as a pale yellow solid.

The above compound (1.58 g) was purified further by sequential chromatography on neutral alumina eluting first with methylene chloride to remove solvent front and high R_f impurities and, subsequently, with methylene chloride/methanol (14:1) to give a pale yellow solid with R_f 0.22 (0.6 g, 38% yield). CHN Analysis: Found (%): C, 41.90; H, 4.01; N, 3.37; S, 7.53. C₁₁₆H₁₂₄N₈S₈O₁₂F₆₈. Theory (%): C, 41.33; H, 3.71; N, 3.33; S, 7.61.

Instrumentation Used for Supercritical Fluid Extraction

Extractions were performed using an Isco SFX[®] supercritical fluid extraction system (Isco Inc., USA, supplied by Jones Chromatography, UK). The SFE system was controlled by the 260D Series Pump controller and consisted of a syringe pump and heated extractor block. A heated variable restrictor was used and the flow rate was set at 1.0 ml min⁻¹. Extracted samples were collected in a liquid-trap containing MIBK or DMSO. The various working pressures were recorded in atmospheres and the temperature of the extractor was set manually. Analysis and detection of extracted samples were carried out using a Pye Unicam SP9 atomic absorption spectrometer and unmodified SF-CO₂ was used for all extractions.

Solubility Measurements of Ligands in Supercritical CO₂

Solubility measurements of each reagent were carried out using the Isco SFE system. A weighed amount (*ca* 80 mg) was placed in an open-ended glass tube (3 x 0.5 cm i.d.). The sample tube was plugged with glass wool at both ends and inserted into the extraction cell (2.5 ml) reducing the volume of the cell to 2.2 ml. The sample was statically extracted at 60°C under 200 or 300 atm of SF-CO₂ for 30 min. After this time, the fluid was vented into a collection vial containing 5 ml of MIBK or DMSO. The sample tube was removed from the cell and weighed. The solubility was calculated from the loss in weight of the sample tube divided by the volume of the extraction cell and given in terms of mmol of sample per litre of CO₂.

SFE of Au(III) from Solid Supports

Cellulose filter paper is a convenient material for studies of the metal extractive ability of designed reagents using supercritical fluid extraction. For the SFE of gold, 40 μl of gold (1000 ppm gold (III) chloride standard) was spiked onto the filter paper (3x1cm). The filter paper was allowed to dry in air for 30 min and was then loaded into the glass tube along

with 20 or 30 mg of the ligand as indicated. The glass tube was plugged with glass wool at both ends and also between the ligand and the filter paper. The glass tube was mounted inside a stainless steel extraction vessel, tightened into the heating block and statically extracted using unmodified SF-CO₂ for 30 min at 400 atm, with temperature varied from 60 to 120°C. The extraction cell was then vented into a collection vessel containing 5 ml of DMSO or MIBK for 15 min (dynamic extraction). Calixarene reagents C2, C3 and C4 are soluble in MIBK while C1 is soluble in DMSO. Having established the optimum temperature for each ligand, the pressure was then varied between 200 and 400 atm. Collected extracts were analysed by flame atomic absorption spectrometry (FAAS). The percentage gold extracted was determined by direct comparison with collecting solutions spiked with standard Au(III) solution.

The extraction was also studied as a function of the amount of water added to the spiked Au(III) on the filter papers. The filter papers were allowed 30 min to air dry after the metal spike and were subsequently each spiked with different amounts of water (0 – 40 ml). Extractions were then carried out under optimum conditions, as described above. Finally extractions were carried out on mg samples of solid Au(0) placed in the extraction cell instead of spiked filter paper. Au(0) can be obtained in mg quantities from the standard Au(III) solution by reduction and heating or by the addition of hydroxylamine hydrochloride. The effect of adding microlitre volumes of standard Fe(III) in HCl solution as an oxidant onto the reduced gold solid was followed by FAAS analysis of collected extracts.

RESULTS AND DISCUSSION

Macrocyclic ligands have received particular attention, as host molecules, since the pioneering work of Pedersen on the synthesis and metal extraction properties of crown ethers. His work began a revolution in macrocyclic ligand and receptor design which continues today as newer host molecules, such as the calixarenes, with unique selectivities of binding and mechanisms of release are produced. The concepts that the cavity size and shape in these macrocycles could be tailor-made and fine-tuned to suit the selected metal cation diameter and that donor atom choice determines the cation selectivity, have caught the imagination of many chemists over the last thirty years. In particular separation scientists have been quick to demonstrate selective metal extractions, using

techniques of liquid-liquid extraction, solid phase and membrane extraction. Our laboratory has previously reported the selective supercritical fluid extraction of Fe(III) from metal mixtures using fluorinated molecular baskets and linear monohydroxamate reagents (22, 23).

The schematic diagram shown below illustrates how such macrocyclic reagents, when sufficiently soluble in supercritical CO₂, can be used to permeate through a solid matrix, sequester the targeted metal and deposit it in a collection vessel. This paper examines the use of new fluorinated calixarenes, aptly named 'molecular baskets' for the selective supercritical fluid extraction of gold.

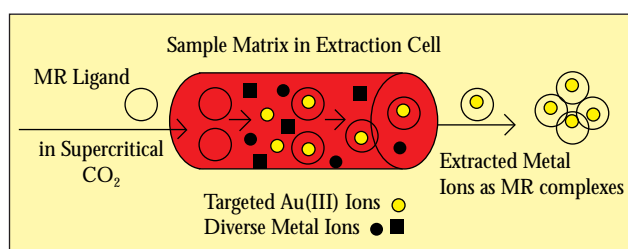


Figure 3 Schematic diagram of SFE of Au ions using macrocyclic extractants

Initially, the solubilities of the reagents were determined in unmodified SF-CO₂ using the method of weight loss described in the experimental section, at 60°C and 200 atm and also at 60°C and 300 atm. The presence of a fluorinated side chain greatly improves the solubility of the calixarenes. For C2 – C4, measured solubilities (mmol/L) were 0.12, 0.13, 0.74 at 60°C, 200 atm increasing to 2.31, 0.29 and 1.96 at 60°C, 300 atm, respectively.

The selective extraction of Fe(III) in unmodified SF-CO₂ from a mixture with other metal ions spiked on cellulose paper, has been demonstrated previously using C1. Here, using Au(III) spiked onto paper, with the pressure set at 400 atm, extractions were carried out with the temperature varied between 60 and 120°C. The extract using C1 was collected in DMSO and the extracts involving the other reagents C2, C3 and C4 were collected in MIBK. Collected extracts were analysed at the ppm level for Au(III) by FAAS (Figure 4). No gold extraction was recorded for C1 under the above conditions. This result was expected for C1. Apart from the calixarene thiol C3, the synthesized calixarenes are expected to form charged complexes with Au(III). The extraction of gold especially at the levels obtained for C4 is thus surprising and as suggested by Wai, the involvement of counter ions is suspected.

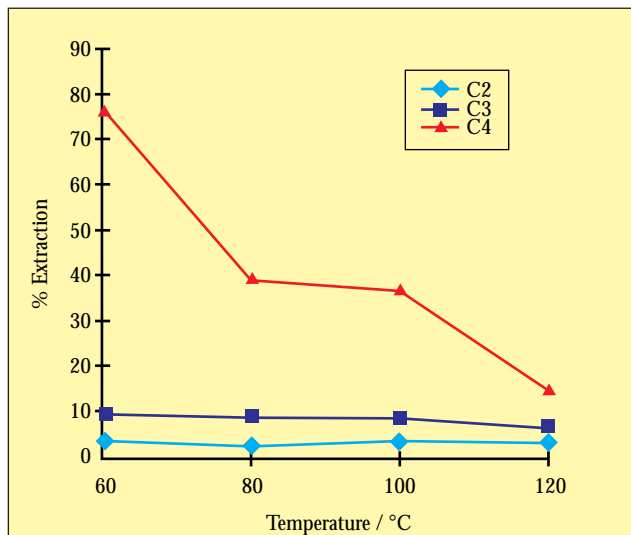


Figure 4 Effect of temperature on the SFE of gold from filter paper at a pressure of 400 atm using synthesized fluorinated tetrameric calixarenes (20 mg reagent, 40 μ l Au(III) standard, 30 min static, 15 min dynamic)

With the optimum temperature of 60°C, the pressure was then varied between 200 and 400 atm (Figure 5). No extraction of gold was again recorded with C1; however, some gold was extracted with C2 (ca 17%) and C3 (ca 9%) at the optimum conditions, 60°C, 200 atm and 60°C and 400 atm, respectively. Much higher extractions were recorded with the thiourea calix[4]arene, C4. All of the C4 reagent was observed to be removed from the extraction cell during SFE carried out at 400 atm.

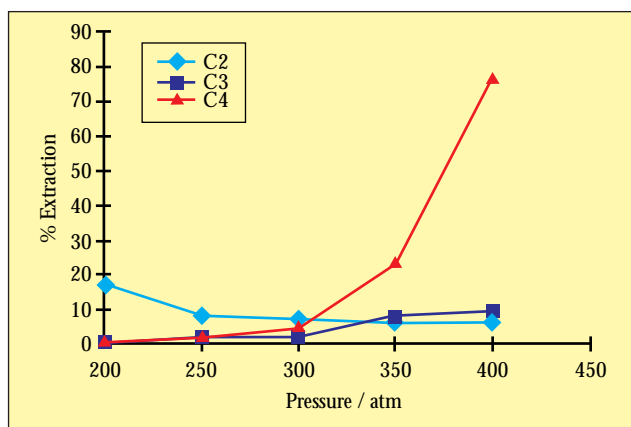


Figure 5 Effect of pressure on the SFE of gold using synthesized fluorinated tetrameric calixarenes at their optimum temperatures (40 μ l Au(III) standard, 20mg ligand, 30 min static, 15 min dynamic)

The effect of spiking water on the filter paper alongside the Au(III) was also studied. Several authors have studied the beneficial effects of water on the extraction of metal ions in SF-CO₂ (6). The filter paper was spiked with different amounts of water (0 – 40 μ l) prior to extraction with each reagent. Again C1 extracted none of the gold. The addition of water had a much smaller effect than pressure variation and for C2 and C4 actually decreased the amount of gold extracted by more than 16%. However, the opposite trend was observed for the ligand C3 where, the percentage extraction was seen to increase from ca 9% to ca 10% when 40 μ l of water was spiked on to the filter paper prior to extraction.

CONCLUSIONS AND FUTURE WORK

Extraction of gold(III) by the fluorinated calix[4]arene thiourea derivative is demonstrated on an analytical scale using supercritical CO₂. No organic solvent modification is needed. High extraction percentages were obtained and as found by other workers in the field of metal extraction by SFE, it is expected that quantitative extraction is achievable through the incorporation of additional washing steps to recover gold after each SFE run. Other fluorinated calix[4]arenes, functionalized on the lower rim with thiol and thioamide groups, were much less efficient. No extraction of gold is possible when Au(0) is used, unless an oxidant is added to the extraction cell. Addition of Fe(III) in acidic solution onto reduced gold in the extraction cell, does however revive the extraction of gold. Further work is in progress on selectivity, reagent recovery and metal release, and on the use of these promising fluorinated reagents for the extraction of gold from geological and material sources.

ACKNOWLEDGEMENTS

Research grant support from Enterprise Ireland through the Basic and Strategic Research Programmes is gratefully acknowledged, as is the support in-kind of industrial partners.

ABOUT THE AUTHORS

Jeremy D Glennon is a graduate of the National University of Ireland, having obtained BSc and PhD degrees in chemistry from University College Dublin. He is director of the Advanced Separations Group in Analytical Chemistry at University College Cork

(UCC), which is dedicated to the study and development of separation and sensing methods using molecular recognition chemistries, clean technology and miniaturisation. Innovative chemistries are being developed which will replace environmentally unfriendly processes involving solvents or hazardous chemicals. In particular toxic metals are targeted for extraction and analysis, alongside recoverable precious metals (gold, silver) from environmental samples, industrial waste and products.

Stephen John Harris is a senior research associate at UCC, receiving a BSc(Hons) in chemistry from the University of California (Berkeley) and his PhD degree from the University of Sussex in the field of organometallic synthesis. He has substantial research and development expertise, gained in industry at Loctite (Ireland) and at Dublin City University and University College Cork. He was visiting professor at the Weizmann Institute of Science in 1991 and has a specialist knowledge of calixarene design and synthesis, recognised in 1987 with Loctite's 'Vernon Kreble Award'. Conor C. McSweeney and Mark P. O'Connell are PhD postgraduate researchers, while Andrew Walker is a graduate of Queens University Belfast and contributed in organic synthesis through a postdoctoral fellowship at UCC.

REFERENCES

- 1 T. Clifford and K. Bartle, *Chemistry in Britain*, 1993, 499
- 2 G. Brunner, in 'Proceedings of the 5th Meeting on Supercritical Fluids, Materials and Natural Products Processing', International Society for the Advancement of Supercritical Fluids, 23-25 March 1998 (Nice, France), Vol. 2, pp. 413-424
- 3 B. Wenclawiak and F.Z. Bichmann, *Anal. Chem.*, 1984, **319**, 305
- 4 C. Fujimoto, H. Yoshida and K. Jinno, *J. Microcolumn Separations*, 1990, **2**, 146
- 5 Y. Lin, R.D. Brauer, K.E. Laintz and C.M. Wai, *Anal. Chem.*, 1993, **65**, 2549
- 6 (a) Y. Lin and C.M. Wai, *Anal. Chem.*, 1994, **66**, 1771
(b) C.M. Wai and S. Wang, *J. Chromatography A*, 1997, **785**, 369
- 7 C.E. Housecroft, *Coord. Chem. Rev.*, 1992, **115**, 117
- 8 R.V. Parish, *Interdisciplinary Science Reviews*, 1992, **17**, 221
- 9 F.A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry, A Comprehensive Text', 4th Edition, John Wiley and Sons, New York, 1980, pp. 966-980
- 10 H. Colley, 'Studies in a Rich Vein', *Chemistry in Britain*, 1992, 720
- 11 (a) H. Schmidbaur, *Interdisciplinary Science Reviews*, 1992, **17** (3), 213
(b) A. Sigel and H. Sigel in 'Handbook on Metals in Clinical and Analytical Chemistry', ed. H.G. Seiler, 1994, p. 388
- 12 C.K. Chen, T.N. Lung and C.C. Wan, *Hydrometallurgy*, 1980, **5**, 207
- 13 C.C. Kenna, *Gold Bull.*, 1991, **24** (4), 126
- 14 D.R. Nagaraj, US Patent 5126038, June 30, 1992, American Cyanamid Company
- 15 V.V. Yakshin, O.M. Vilokova and N.A. Tsarenko, *J. Anal. Chem.*, 1994, **49**, 158
- 16 S. Fang and L. Fu, *Ind. J. Chem.*, 1994, **33A**, 885
- 17 M. Trom, M. Burgard and A. El-Bachiri, *Analysis* 1991, **19**, 97
- 18 M. Trom, M. Burgard, M.J.F. Leroy and M. Prevost, *J. Membrane Sc.*, 1988, **38**, 295
- 19 (a) R.L. Bruening, B.J. Tarbet, T.E. Krakowiak, M.L. Bruening, R.M. Izatt and J.S. Bradshaw, *Anal. Chem.*, 1991, **63** (10), 1014
(b) R.L. Bruening, B.J. Tarbet, K.E. Krakowiak, R.M. Izatt and J.S. Bradshaw, *J. Heterocyclic Chem.*, 1990, **27**, 347
- 20 S. Wang, S. Elshani and C.M. Wai, *Anal. Chem.*, 1995, **67**, 919
- 21 E.O. Otu, *Separation Science and Technology*, 1997, **32** (6), 1107
- 22 J.D. Glennon, S. Hutchinson, C.C. McSweeney, S.J. Harris and M.A. Mc Kervey, *Anal. Chem.*, 1997, **69** (11), 2207
- 23 J.D. Glennon, S. Hutchinson, A. Walker, S.J. Harris, and C.C. McSweeney, *J. Chromatography A*, 1997, **770**, 85

Continued from page 51

REFERENCES

- 1 M. Malte-Brun, 'Universal Geography', Wells and Lilly, 1824
- 2 E.E. Lungwitz, *Min. J. Lond.*, 1900, 318
- 3 L.V. Razin and I.S. Rozhkov, 'Geochemistry of Gold in the Weathering Crust and the Biosphere of Kuranakh-type Gold Ore Deposits' (in Russian), Izdat. Nauka, Moscow, 1966
- 4 R.S. Jones, *U.S. Geol. Surv. Circ.*, 1970, **625**, 1970
- 5 H.T. Shacklette, H.W. Lakin, A.E. Hubert and G.C. Curtin, *U.S. Geol. Surv. Bull.*, 1970, **1314-B**, B1
- 6 R.W. Boyle, *Geol. Surv. Can. Bull.*, 1979, **280**, 1
- 7 R.R. Brooks, *J. Geochem. Explor.*, 1982, **17**, 109
- 8 C.E. Dunn, in 'Noble Metals and Biological Systems', ed. R.R. Brooks, CRC Press, Baton Raton, 1992
- 9 J.A. Erdman and J.C. Olson, *J. Geochem. Explor.*, 1985, **24**, 281
- 10 H.V. Warren and R.E. Delavault, *Geol. Soc. Amer. Bull.*, 1950, **61**, 123
- 11 R.R. Brooks, J. Lee, R.D. Reeves and J. Jaffré, *J. Geochem. Explor.*, 1977, **7**, 49
- 12 C.W.N. Anderson, R.R. Brooks, R.B. Stewart and R. Simcock, *Nature*, 1998, **395**, 553
- 13 B. Nemeč, L. Babicka and A. Oborsky, *Int. Acad. Bohème Sci. Bull.*, 1936, **37**, 1
- 14 H.L. Cannon, H.T. Shacklette and H. Bastron, *U.S. Geol. Surv. Bull.*, 1968, **1278A**, 1
- 15 R.R. Brooks, J. Holzbecher and D.E. Ryan, *J. Geochem. Explor.*, 1981, **16**, 21
- 16 S.P. McGrath, C.M.D. Sidoli, A.J.M. Baker and R.D. Reeves, in 'Integrated Soil and Sediment Research: a Basis for Proper Protection', ed. J.P. Eijsackers and T. Hamers, Kluwer, Dordrecht, 1993
- 17 R.L. Chaney, in 'Land Treatment of Hazardous Wastes', ed. J.F. Parr *et al.*, Noyes Data Corporation, 1983
- 18 R.R. Brooks, M.F. Chambers, L.J. Nicks and B.H. Robinson, *Trends Pl. Sci.*, 1998, **3**, 359
- 19 M.J. Blaylock *et al.*, *Environ. Sci. Technol.*, 1997, **31**, 860
- 20 R.M. Talipov, V.M. Glushchenko, N.D. Lezhneva and P.Kh. Nishanov, *Uzbek. Geol. Zhur.*, 1974, **No.4**, 168
- 21 C.A. Girling and P.J. Peterson, *Gold Bull.*, 1980, **13**, 151
- 22 L.J. Nicks and M.F. Chambers, in 'Plants that Hyperaccumulate Heavy Metals', ed. R.R. Brooks, CAB International, Wallingford, 1988
- 23 C.H. Hung and S.G. Pavlostathis, *Water Res.*, 1997, **31**, 2761
- 24 C. French, personal communication