The Analyst

Extraction and recovery of metals using a supercritical fluid with chelating agents

Mark D. Burford,[a] Mustafa Z. Ozel,[a] Anthony A. Clifford,[a] Keith D. Bartle,[a] Yuehe Lin,[b] Chien M. Wai[b] and Neil G. Smart[c]

[a] *Department of Chemistry, Leeds University, Leeds, UK LS2 9JT*
[b] *Department of Chemistry, University of Idaho, Moscow, Idaho 83843, USA*
[c] *BNFL, Sellafield, Seascale, Cumbria, UK CA20 1PG*

Received 18th November 1998, Accepted 4th February 1999

The supercritical fluid extraction (SFE) of metal ions was assessed in terms of the ability of the process to extract, solvate, transport and collect metal species. The extraction efficiency (per cent removed from the sample matrix), collection efficiency (per cent recovered in the collection solvent) and SFE residue (unextracted metal complex or metal ion recovered from the apparatus by flushing with an organic or acidic solvent, respectively) were determined to ascertain whether a mass balance for the metal could be achieved. Using this approach, it was demonstrated that the amount of metal extracted from the sample matrix did not necessarily correspond to the concentration of metal recovered in the collection solvent, as the chelated metal complex could partially degrade and/or dissociate in the supercritical fluid prior to collection. Typically, a discrepancy of 1 to 15% could be obtained. The non-fluorinated metal β-diketones and dithiocarbamates had a greater tendency to dissociate and/or degrade in a supercritical fluid (*i.e.*, *ca.* 14 and 5%, respectively) than the corresponding fluorinated metal complex (*i.e.*, *ca.* 6 and 1%, respectively). As for the collection solvents, a range of suitable fluids were found to be capable of obtaining quantitative metal complex recoveries, including methanol, chloroform, isobutyl methyl ketone or 10% nitric acid. A radioactive isotope, ^{177}Lu, was used to trace the location of the metal residue in the SFE apparatus.

Introduction

Supercritical fluid extraction (SFE) is becoming an increasingly popular technique for the extraction and recovery of a wide range of organometallic and inorganic analytes from real world samples. The most common supercritical fluid (SF), carbon dioxide, can efficiently extract neutral organometallic compounds, such as tetraalkyltin,[1] but the direct extraction of metal ions has proved far less successful, as charge neutralisation of the ion (*e.g.*, by chelation) is required to significantly enhance the solubility of the metal in an SF. Typical chelating agents used in SFE include dithiocarbamates,[2–5] β-diketones,[6,7] tributyl phosphate[8] and crown ethers.[9]

To use SFE as an analytical or industrial scale process, both the extraction and collection efficiency of the procedure need to be determined. The collection efficiency (per cent recovered in the collection solvent) is assessed by spiking the analyte to be collected (*e.g.*, the organometallic compound or metal complex) onto an inert matrix and extracting the sample with CO_2. The recoveries obtained are an indication of whether the analyte has been adequately flushed from the extraction cell and quantitatively retained in the collection device. The extraction efficiency (per cent removed from the sample matrix) is calculated on the basis of the amount of analyte present in the sample matrix before and after extraction. The removal of metal from the sample matrix is an indication of the ability of the ligand to complex and solvate the metal ion and overcome matrix–analyte interactions.

At present, the SFE metal recoveries are reported as either the per cent recovered in the collection solvent or the per cent removed from the sample matrix. For example, the organometallic compounds, such as alkyltin,[1,10] alkyllead,[11] and dimethylarsinic acid,[12] have been assessed in terms of the per cent recovered from spiked[1,10,11] and real world[10,12] samples using aqueous[12] or organic[1,10,11] collection solvents. Conversely, the extraction of metal ions is usually determined as the per cent removed from the sample matrix,[3,6–8] although some collection data are available using on-line atomic absorption spectroscopy[4,13] and off-line collection into aqueous[13] or organic[5,14] solvents. When both the extraction and collection efficiency of the process are assessed, a discrepancy between the two values may be obtained, suggesting that some of the metal has been ‘held up’ within the extraction apparatus.[15]

The quantitative extraction and recovery of metal complexes by SFE has proved to be more difficult than initially anticipated. This is because unlike organic analytes, which once solvated in the SF can easily be transferred to the collection device,[16,17] the metal chelates are prone to dissociation and decomposition.[5,18,19] Several metal chelates dissociate or thermally decompose in SF CO_2,[15,18,19] the exposed metal ion irreversibly binding to the stainless steel vessel and remaining in the extraction apparatus.[20] Fewer contamination problems were obtained when using polyether etherketone (PEEK) extraction equipment,[5] but the procedure has a lower working temperature and pressure range (*e.g.*, 50 °C and 200 atm).[7]

SFE metal recoveries can also be hindered by the low solubility of several of the metal complexes in SF CO_2. This means that, during the depressurisation of the extract into the collection device, the metal complexes have a greater tendency to precipitate and plug in the restrictor. Unlike organic analytes, heating the restrictor often does not eliminate the plugging as many of the complexes are non-volatile and/or thermally labile. An alternative collection method is to use pressure rather than temperature to overcome the plugging problems associated with the metal chelates.[21] Several of the metal complexes can also polymerise under SFE conditions,[22] and this may reduce the solubility of the complexes and hence their recovery from the sample matrix.

The aim of this study was to ensure that a mass balance could be obtained for the metal before and after SFE. Thus, if non-quantitative recoveries were obtained, it would be possible to ascertain if this was due to poor extraction efficiencies, poor collection efficiencies or the dissociation of the metal complex within the extraction apparatus. Two approaches were investigated: (i) a sequential extraction method in which the apparatus was flushed with a series of solvents to determine the type of metal residue in the extraction appartus; (ii) a radioisotope (^{177}Lu) was extracted with commercial complexing agents to study the SF chelation and recovery of the metals *in situ*.

Experimental

Standards and samples

Acetylacetone (AA), hexafluoroacetylacetone (HFA), sodium diethyldithiocarbamate (NaDDC) and tributyl phosphate (TBP) were purchased from Aldrich Chemical Co. (Milwaukee, WI, USA) and used without further purification. Lithium bis(trifluoroethyl)dithiocarbamate (FDDC) was synthesised according to the procedure outlined in the literature.[23] The aqueous 1000 ppm metal ion solutions of Co^{2+}, Cd^{2+}, Pb^{2+} and Lu^{3+} (Aldrich) were used as received. Cobalt(II) acetylacetonate (Aldrich) and cobalt(II) hexafluoroacetylacetone (Aldrich) were prepared in methanol (1 mg ml^{-1}) and stored at 6 °C until used. Lead(II) diethyldithiocarbamate and lead(II) trifluoroethyldithiocarbamate (obtained using conventional solvent/ligand extraction and purification) were prepared in methylene chloride (1 mg ml^{-1}) and stored at 6 °C until used. The sample matrices, namely No. 1 Whatman filter paper (Whatman, Maidstone, UK), 70–80 mesh silanised glass beads (Analab, Norwalk, CT, USA) and sea-washed sand (Alltech, IL, USA), were used as received. All other chemicals used were analytical grade reagents. The radioisotope ^{177}Lu (E_r = 208 keV, $t_{\frac{1}{2}}$ = 6.7 d) was produced by neutron activation. The solution containing 2.0×10^{-3} M Lu^{3+} in 0.01 M nitric acid was irradiated for 1 h in a 1 MW Trigar nuclear reactor at a steady flux of 6×10^{12} neutrons cm^{-2} s^{-1}. After irradiation, the pH of the solution was adjusted to *ca.* 4.0 by adding sodium acetate.

Apparatus

In this study, two types of extraction apparatus were constructed, one for the extraction of heavy metals (System 1) and the other for use with the radioactive isotope ^{177}Lu (System 2).

System 1. Supercritical fluid extractions were performed using industrial CP grade carbon dioxide (BOC Ltd, London, UK) with an ISCO Model 260D sge pump (ISCO, Lincoln, NE, USA) operated at 400 atm. The 0.5 or 3.5 ml extraction cells (Keystone Scientific, Bellefonte, PA, USA) and a pre-equilibration coil [1 m × 0.76 mm id × 1.6 mm (1/16 in) od] were maintained at 60 °C (±0.1 °C) using a Carlo Erba (Milan, Italy) Fractovap gas chromatograph oven. The extraction cell was connected to the SFE apparatus using 'slip-free', finger tight connectors (Key Scientific). The flow rate of the SF through the extraction cell was measured as liquid CO_2 at the pump and was controlled by an 18 cm length × 50 μm id × 375 μm od fused silica restrictor (Polymicro Technologies, Phoenix, AZ, USA). At 400 atm and 60 °C, a flow rate of *ca.* 2 ml min^{-1} was obtained. Extracted analytes were collected in a 21 ml vial containing 10 ml of methanol, chloroform, isobutyl methyl ketone (IBMK) or 10% nitric acid. No attempt was made to control the collection solvent temperature during SFE, but the collection solvent volume was maintained during the extraction by adding further solvent to the collection vial.

System 2. Supercritical fluid extractions were performed using a premixed SFC grade CO_2–5% methanol mixture (Scott Speciality Gases, Plumsteadville, PA, USA) with a cooled Haskel pump (Haskel Inc., Burbank, CA, USA) operated at 200 atm. The extraction pressure was monitored and controlled to within ±5 psi using a Setra System (Acton, MA, USA) pressure transducer and a microprocessor based controller. The 3.5 ml extraction cell (Dionex, Sunnyvale, CA, USA) and 3.5 ml pre-equilibration cell were maintained at 60 °C (±0.1 °C) using a fan assisted oven controlled by an Omega (Stamford, CT, USA) BS5001J1-A temperature controller. Several linear flow restrictors were used to maintain the extraction flow rate, namely: (i) a 48 cm length × 50 μm id × 375 μm od fused silica restrictor supplied by J&W Scientific, Folsom, CA, USA; and (ii) a 48 cm length × 50 μm id × 375 μm od fused silica restrictor inserted into a 47 cm length × 0.51 mm id × 1.6 mm (1/16 in) od PEEK tube (Upchurch Scientific, Oak Harbor, WA, USA). The flow rate of the SF was measured as a gas and was *ca.* 1.4 ml min^{-1} at 60 °C and 200 atm. The extracts were depressurised into a 15 ml vial containing 6 ml of IBMK.

Procedure

To evaluate both the extraction and collection efficiency of the SFE process, several analyses were undertaken, namely: (i) determination of the metal concentration on the sample matrix before and after SFE; (ii) assessment of the type and amount of metal residue remaining in the SFE apparatus after extraction; and (iii) determination of the concentration of metal recovered in the collection solvent. The location of the metal residue in the apparatus was assessed by extracting a radioactive isotope and, on completion of the extraction, using a Geiger–Müller counter to detect and locate the radioactive residue in the SFE apparatus. These various methods used to obtain a mass balance for the spiked metals are given below.

Collection efficiency. Using a micropipette, the metal complex (1 μmol) was spiked onto 1 g of 100 μm od silanised glass beads placed inside a 0.8 ml stainless steel extraction cell. The cell was pressurised to 400 atm CO_2 at 60 °C and the contents dynamically extracted using a flow rate of *ca.* 2 ml min^{-1} for 20 min. The extract was collected in a 21 ml glass vial containing 10 ml of methanol, chloroform, IBMK or 10% nitric acid. Following depressurisation, 10 ml of chloroform and then 10 ml of 10% nitric acid were pumped through the extraction apparatus at room temperature and pressure using Merck–Hitachi LC660 pumps (Merck–Hitachi, Wokingham, UK). Any residual nitric acid was removed from the apparatus by pumping methanol through it and then flushing the equipment with 400 atm CO_2 at 60 °C. Extracts were analysed using a Varian Spectra AA-10 flame atomic absorption spectrometer with an air–acetylene flame. Methanol, IBMK and nitric acid extracts were analysed directly. Chloroform extracts were evaporated and redissolved in 10 ml 10% nitric acid prior to flame atomic absorption spectrometry (FAAS) analysis.

Extraction efficiency. The extraction efficiency of the SFE process was assessed using both a non-fluorinated and fluorinated β-diketone to extract cobalt from a model matrix, namely filter paper. Using a micropipette, Co^{2+} (0.9 μmol) was spiked onto 2 cm × 2 cm No. 1 Whatman filter paper (Whatman, Maidstone, UK) and dried for 3 h at 130 °C. The dried, spiked matrix was placed on a bed of silanised glass wool situated inside a 3.5 ml stainless steel extraction cell. An aliquot of 100 μmol of HFA or AA was placed directly on top of the spiked filter paper, followed by 10 μl of distilled water and the remainder of the cell volume was occupied with additional silanised glass wool. The cell was pressurised with 400 atm CO_2 at 60 °C and left to equilibrate for 20 min. A dynamic extraction was carried out using SF CO_2 at a flow rate of *ca.* 2 ml min^{-1} for 20 min. Extracts were collected in 10 ml of methanol in a 21 ml vial. After depressurisation, the sample matrix was removed from the extraction cell and placed in a 10 ml PEEK vessel (Phase Separations Ltd, Clwyd, UK), which was sequentially flushed with 10 ml of chloroform and 10 ml of 10% nitric acid at room temperature and pressure using Merck–Hitachi LC660 pumps. Similarly, the SFE apparatus was flushed with 10 ml of chloroform followed by 10 ml of 10% nitric acid using the HPLC pumps. Extracts were analysed by FAAS.

The extraction efficiency of the SFE process was also assessed using a fluorinated and non-fluorinated dithiocarbamate to extract Co^{3+}, Cd^{2+} and Pb^{2+}. The metal ions (0.85 μmol Co, 0.24 μmol Pb and 0.44 μmol Cd) were spiked onto a sand matrix placed inside a 0.8 ml stainless steel extraction cell, the sand half filling the cell. The spiked matrix was then left for 1 h to air dry. DDC (250 μmol) or FDDC (190 μmol) ligand, along with 50 μl of distilled water, was placed onto the spiked sand and the remainder of the cell was filled with sand. The cell was connected to the SFE apparatus and the SFE procedure (as detailed earlier for the β-diketones) was followed. On completion of the SFE step, the apparatus and cell containing the glass beads were sequentially flushed with 10 ml of methylene chloride and 10 ml of 10% nitric acid using two Merck–Hitachi LC660 pumps. The supercritical fluid extracts were collected in 10 ml of methanol.

Location of metal residue in extraction apparatus. A radioactive isotope of Lu^{3+} was spiked onto a strip of filter paper which was placed inside a glass tube (0.5 cm id × 3 cm length) plugged at one end with glass wool. An additional 10 μl of distilled water was added to the filter paper along with 211 μmol HFA, 20 μl TBP and 20 μl methanol. The open end of the glass tube was sealed with glass wool and immediately placed inside the 3.5 ml extraction cell. The cell was pressurised with 200 atm CO_2 at 60 °C and left to equilibrate for 10 min. The cell was dynamically extracted with SF CO_2 at a flow rate of *ca.* 1.4 ml min^{-1} for 15 min. The extract was collected in 6 ml of IBMK in a glass vial.

Upon completion of the SFE step, the filter paper was removed from the cell and the metal residue was analysed using an Ortec (Oak Ridge, TN, USA) Ge(Li) detector with a resolution (full width at half maximum) of approximately 2.3 keV at the 1332 keV ^{60}Co peak. A filter paper containing the same amount of irradiated Lu^{3+} ions was used as a standard and counted under identical conditions. The extraction efficiency, expressed as the per cent removed, was based on the amount of Lu^{3+} found on the filter paper before and after extraction. The IBMK collection solvent was transferred to a PEEK bottle and counted in the Ge(Li) detector to determine the amount of metal recovered from the apparatus. A 6 ml nitric acid solution containing 5 μl of irradiated Lu^{3+} ions was used as a standard for 100% recovery. Following each extraction, a portable Geiger–Müller counter (Model PUG-1, Technical Associates, Burbank, CA, USA) was used to trace the radioactivity in the SFE apparatus. Each part of the extractor was disconnected and sequentially washed with IBMK and 50% nitric acid, and the radioactivity of the solvent washings was determined using the Ge(Li) detector.

Results and discussion

The collection efficiency of the process was evaluated in terms of the metal complex recovered, so that only the transport and collection of a spiked metal complex from the extraction cell to the collection device were studied. The extraction efficiency was assessed in terms of the ability of a ligand to chelate and solvate a spiked metal ion from a sample matrix. The success of the extraction was based on the amount of metal removed from the sample. To ensure that a mass balance was achieved, the extraction apparatus was flushed with an organic and acidic solvent to recover any metal residue, the location of which could be ascertained by means of a radioactive tracer.

Collection efficiency of SFE process

At present, only a limited amount of information is available on the SFE collection efficiency of metal complexes. Various collection solvents have previously been used to trap the metal chelates, including water,[13] ethanol,[14] chloroform[7] and IBMK,[5] but as yet no comparison between the various collection methods has been undertaken. In this study, the collection conditions were optimised by assessing the recovery of several fluorinated and non-fluorinated β-diketone and dithiocarbamate metal complexes from an inert matrix (*e.g.*, silanised glass beads) as shown in Tables 1 and 2.

The results in Table 1 show that, regardless of the collection solvent used, only *ca.* 75% of the $Co(AA)_2$ β-diketone metal complex was recovered. The non-quantitative metal $Co(AA)_2$ recoveries were initially thought to be related to the poor trapping efficiency of the collection solvents, but, on sequentially flushing the extraction apparatus with chloroform (*e.g.*, to recover the unextracted metal complex) and then 10% nitric acid (*e.g.*, to recover the metal ion), a quantitative mass balance could be achieved. From the results, it appears that the metal complex has sufficient solubility in the supercritical CO_2 to be solvated and flushed from the apparatus since only *ca.* 2% of the complex remained in the apparatus following the extraction. This was expected as $Co(AA)_2$ has a relatively high solubility in CO_2 enabling the complex to be recovered during the dynamic extraction step.[24] The poor metal recoveries are therefore related to the degradation and/or metal exchange of the complex during SFE, as the remainder of the metal was recovered upon flushing the apparatus with 10% nitric acid. To accurately assess the collection efficiency of the various solvents, a total recovery of the metal (*e.g.*, including the SFE residue) was used.

For the fluorinated β-diketone metal complex, namely $Co(HFA)_2$, a more efficient supercritical fluid recovery was achieved in the region of 85%. This slight increase in the

Table 1 Collection efficiency of $Co(AA)_2$ and $Co(HFA)_2$ metal complexes in several collection solvents

	$Co(AA)_2$ recovery (%)[a]				$Co(HFA)_2$ recovery (%)[a]
Location of analyte	10% HNO_3	Chloroform	IBMK	Methanol	Methanol
Metal residue in SFE system					
Flushed with $CHCl_3$	1.1 ± 0.6	1.4 ± 1.1	0.7 ± 0.3	4.1 ± 5.2	0.1 ± 0.1
Flushed with 10% HNO_3	21.9 ± 5.0	18.8 ± 3.8	11.2 ± 2.4	9.5 ± 1.5	8.8 ± 2.9
Metal in collection solvent	69.1 ± 6.7	71.3 ± 4.0	79.8 ± 8.7	81.7 ± 11.6	86.4 ± 2.9
Total	92.1 ± 2.3	91.5 ± 1.0	91.7 ± 6.8	95.3 ± 8.1	95.3 ± 1.9

[a] Recovery of triplicate analysis. Dynamic extraction of metal complex from silanised glass beads using 400 atm, 60 °C CO_2.

recovery of the fluorinated metal complex relative to the corresponding non-fluorinated metal complex is probably due to the enhanced thermal stability of the fluorinated complex.

The supercritical fluid recovery of metal dithiocarbamates was also investigated as shown in Table 2. Lead diethyldithiocarbamate [$Pb(DDC)_2$] proved to be the most difficult complex to recover as, on average, less than 55% of the material was collected in the various collection solvents investigated. Again, the non-quantitative metal complex recoveries were initially thought to be related to the poor trapping efficiency of the collection solvents, but, on sequentially flushing the extraction apparatus with an organic and acidic solution, a quantitative mass balance could be achieved. From the results it appears that the metal complex has some solubility limitations as, on average, *ca.* 15% of the metal complex remains in the cell. The non-fluorinated metal dithiocarbamates have a relatively low solubility in supercritical carbon dioxide,[25] and so there may be insufficient solubility to enable the complex to be quantitatively recovered in the supercritical fluid.

The poor metal recoveries are also related to the degradation and/or metal exchange of the complex during the SFE step, as the remainder of the metal, namely *ca.* 37%, was recovered upon flushing the apparatus with 10% nitric acid. Although not investigated in detail, a detectable odour of carbon disulfide was observed from the collection solvents and from the sample matrix after the extraction, carbon disulfide being one of the major degradation products of the dithiocarbamates.[26] It has also been demonstrated that the $Pb(DDC)_2$ metal complex is relatively unstable and can undergo substitution reactions with nickel from the stainless steel in the analytical apparatus.[27]

Conversely, the fluorinated $Pb(FDDC)_2$ complex had a near quantitative SFE recovery as *ca.* 87% of the metal complex was recovered in the collection solvent. The enhanced recoveries were related to the increased stability of $Pb(FDDC)_2$ in the supercritical fluid[18] and the enhanced solubility of the fluorinated dithiocarbamate metal complexes in carbon dioxide.[28] Thus, only *ca.* 4% of the metal complex was recovered by flushing the SFE apparatus with methylene chloride. In the region of 12% of the metal complex appears to have degraded and/or dissociated in the SFE apparatus, although this is significantly less than the 37% seen for the non-fluorinated DDC metal complex.

To accurately assess the collection efficiency of the various organic solvents, a total recovery of the metal is used (*e.g.*, including the SFE residue). Chloroform was initially chosen as the collection solvent as it is frequently used in conventional metal solvent extraction. As shown in Tables 1 and 2, total recoveries of more than 90% indicate that chloroform is a suitable collection solvent for SFE applications. However, solutions in chlorinated solvents cannot be directly analysed by FAAS due to their toxicity and corrosive effect on the atomic absorption apparatus. Consequently, prior to analysis, the extract has to be evaporated and redissolved in methanol, or back extracted with 10% nitric acid and then diluted.

Alternative organic and aqueous solvents were investigated which would enable direct analysis of the metal chelates by FAAS. Previous conventional solvent extraction methods have used simple alcohols and ketones, such as methanol and IBMK, to achieve this goal and these organic solvents were also suitable for SFE applications, with recoveries which were comparable with those of chloroform (see Tables 1 and 2). An acidic collection solvent can also be used to dissociate the metal complex enabling collection of the metal ion. In Tables 1 and 2, the collection efficiencies in 10% nitric acid are comparable with those achieved with the organic solvents. However, care must be taken in interpreting these acidic collection solvent results since similar recoveries to the organic solvents are only achieved when the extraction flow rate is $\leqslant 2$ ml min^{-1} (as measured at the pump). It is likely that, at higher flow rates, the metal complex does not have sufficient time to dissociate in the acidic medium, so the undissociated complex is entrained in the CO_2 and lost to the atmosphere as an aerosol.

These investigations of collection efficiency reveal that, although chloroform, IBMK and 10% nitric acid provide satisfactory recoveries, methanol is the most versatile solvent as the extract can be directly analysed by FAAS, UV–visible spectroscopy and various chromatographic techniques.

Extraction efficiency of SFE process

The extraction efficiency of the SFE process was assessed using commercial fluorinated and non-fluorinated β-diketones to extract spiked cobalt from an inert sample matrix, namely filter paper (Table 3), and fluorinated and non-fluorinated dithiocarbamates to extract cobalt, cadmium and lead from a sand matrix (Table 4). All the complexing agents were used in molar excess with a ligand to metal ratio of typically $\geqslant 100:1$. The results in Table 3 show that both β-diketone complexing agents were able to partially extract the cobalt from the filter paper, the AA ligand removing *ca.* 25% of the metal and the HFA ligand *ca.* 70%. For HFA, this extraction efficiency was reflected in the corresponding collection efficiency value of *ca.* 65%. Therefore minimal degradation of the resulting metal complex had occurred in the extraction apparatus. However, for the non-fluorinated ligand, the extraction efficiency was not reflected in the corresponding collection efficiency. In the case of AA, a significant fraction of the spiked metal was extracted from the sample matrix (*i.e.*, 30%); however, virtually none of the resulting metal complex was recovered in the collection solvent (*i.e.*, <2%). This discrepancy between the extraction and collection efficiency data indicated that an appreciable fraction of the extracted metal remained in the SFE apparatus. To investigate this further, sequential solvent flushes were employed using chloroform and 10% nitric acid to recover the metal residue. Analysis of the chloroform extract showed that a very small percentage (*e.g.*, 1–2%) of the metal complex remained in the extraction apparatus, demonstrating that the intact metal complexes had sufficient solubility to be completely flushed from the apparatus. However, the recoveries from the nitric acid extract suggested that a significant fraction of the AA metal complex (*i.e.*, *ca.* 14%) and, to a lesser extent, the HFA metal complex (*i.e.*, *ca.* 6%) had partially or fully dissociated in the extraction apparatus.

Table 2 Collection efficiency of $Pb(DDC)_2$ and $Pb(FDDC)_2$ metal complexes in several collection solvents

	$Pb(DDC)_2$ recovery (%)[a]					$Pb(FDDC)_2$ recovery (%)[a]
Location of analyte	10% HNO_3	Chloroform	CH_2Cl_2	IBMK	Methanol	Methanol
Metal residue in SFE apparatus						
Flushed with CH_2Cl_2	8.7 ± 1.4	6.5 ± 0.1	12.4 ± 5.0	21.4 ± 3.5	18.1 ± 3.0	3.1 ± 0.8
Flushed with 10% HNO_3	39.1 ± 7.2	43.8 ± 0.2	36.2 ± 8.9	33.5 ± 6.0	34.4 ± 3.7	11.9 ± 1.2
Metal in collection solvent	50.8 ± 2.7	53.1 ± 4.5	57.3 ± 10.2	45.8 ± 9.2	56.7 ± 5.6	86.6 ± 1.7
Total	98.6 ± 3.8	103.4 ± 1.6	105.9 ± 8.0	100.7 ± 6.2	109.2 ± 4.1	101.6 ± 1.2

[a] Recovery of triplicate analysis. Dynamic extraction of metal complex from silanised glass beads using 400 atm, 60 °C CO_2.

From Table 3, it is clear that the dissociation of the metal chelate in the SF is much more pronounced for $Co(AA)_2$ than for $Co(HFA)_2$, as *ca.* 44% of the metal complex formed in the SF dissociates or degrades in the extraction apparatus when using AA, as compared with *ca.* 7% when using HFA. The significant difference in the recoveries of the metal complexes is in part due to the greater thermal stability of the fluorinated complex than the non-fluorinated metal chelate, which is prone to thermal decomposition under SF conditions.[29] The fluorinated metal complex has the advantage that it is significantly more volatile than the non-fluorinated analogue, since it has an order of magnitude greater vapour pressure,[30,31] and hence an enhanced solubility in the SF. The presence of two CF_3 groups also increases the acidity of the ligand by four orders of magnitude (*e.g.*, AA pK_a = 8.67, HFA pK_a = 4.46[32]), which enables HFA to extract from a more acidic medium. This reduction in the basic strength of the fluorinated ligand can be an advantage as water (which is generally required in the SFE process to obtain quantitative extraction efficiencies) is strongly acidic (*e.g.*, pH 2.8[33]) under SFE conditions.

It is also apparent that the static time used in the extraction process can be detrimental to the overall recovery of the metal. An increase in static time from 0 to 20 min increases the degradation of the non-fluorinated $Co(AA)_2$ metal complex from *ca.* 15% (Table 1) to ca. 44% (Table 3). No such increase in degradation was seen for the HFA complex which remained at *ca.* 8% for both a 0 min (Table 1) and 20 min (Table 3) static SFE step. Thus, for the non-fluorinated ligand, there will be a compromise between the optimum static time required to attain an equilibrium and the time required to minimise the degradation of the resulting metal chelate. It may be that, for such thermally labile complexes, the AA ligand should be added dynamically throughout the extraction, so that when degradation or dissociation occurs the excess ligand is available to re-complex with the metal ion.

Table 3 Extraction and collection efficiency of SFE process using ß-diketones

	Per cent recovery of cobalt(II)[a]	
Location of analyte	AA	HFA
Metal residue on sample matrix		
Matrix washed with $CHCl_3$	2.0 ± 0.1	1.2 ± 0.5
Matrix washed with 10% HNO_3	75.0 ± 8.6	30.3 ± 4.9
Metal residue in SFE apparatus		
Flushed with $CHCl_3$	3.9 ± 2.0	0.5 ± 0.2
Flushed with 10% HNO_3	13.9 ± 2.3	6.5 ± 2.2
Metal in collection solvent	1.3 ± 0.5	65.3 ± 8.8
Total	96.1 ± 2.2	103.8 ± 5.0

[a] Recovery of triplicate analysis.

In an attempt to improve the recovery of the metal, a non-fluorinated (DDC) and fluorinated (FDDC) dithiocarbamate were investigated, since the dithiocarbamates have previously proved to be very successful in SFE applications.[2,3,5] The results in Table 4 show that the dithiocarbamates exhibit a similar trend to the β-diketones, in that higher collection solvent recoveries are achieved using a fluorinated ligand (*i.e.*, > 90%) rather than a non-fluorinated ligand (*i.e.*, *ca.* 10–15%). However, in this instance, the FDDC ligand was able to efficiently extract the metal ion from the sample matrix, as well as solvate and transport the metal from the sample matrix to the collection device. Hence quantitative SFE recoveries could be achieved with the FDDC ligand. Conversely, for the non-fluorinated DDC ligand, poor extraction efficiencies were obtained, as the majority of the metal ions remained on the sample matrix.

Location of metal residue using a radioactive tracer

It is clear from the previous studies that a quantitative recovery of the metal ion may be hampered by dissociation of the metal complex in the SF. A preliminary *in situ* assessment of the SFE process was undertaken using HFA with TBP and a radioactive tracer ^{177}Lu. Following the SFE of ^{177}Lu, a Geiger–Müller counter was passed along the length of the apparatus. Radioactivity could still be detected within the extraction cell and outlet valve and, to a lesser extent, within the transfer tubing and restrictor. This rapid external assessment of the extraction process was undertaken within minutes of completing the SFE step, and could be used as a screening technique to qualitatively ascertain if the metal has been successfully transferred to the collection device.

To quantitatively determine the concentration of ^{177}Lu remaining in the apparatus, the apparatus was dismantled and the various components sequentially flushed with an organic (IBMK) and aqueous (50% nitric acid) solvent. The results in Table 5 show that the radioactive tracer was quantitatively extracted from the sample matrix, and the majority of the ^{177}Lu remaining in the apparatus was present as the metal complex (*i.e.*, was IBMK soluble). It is probable that the non-quantitative recoveries are related to the configuration of the extraction apparatus. For example, the transport or sweeping of the metal complex out of the extraction cell and into the collection vial was significantly affected by the orientation of the cell, since, on completion of the SFE step, 8% of the complex remained in the horizontal cell compared with less than 1% in the vertical cell (see Table 5). A similar trend was found for the SFE of organic analytes which have a slower rate of extraction from a horizontal cell than from a vertical cell.[34] Note that, for the non-radiotracer work, the cell was in a vertical position.

The location of the outlet valve in the extraction apparatus also affected the recovery of the metal complex, as shown in

Table 4 Extraction and collection efficiency of SFE process using dithiocarbamates

	Per cent recovery[a]					
	DDC			FDDC		
Location of analyte	Co(II)	Cd(II)	Pb(II)	Co(II)	Cd(II)	Pb (II)
Metal residue on sample matrix						
Matrix washed with CH_2Cl_2	3.4 ± 1.0	5.6 ± 3.9	1.2 ± 0.4	0.0 ± 0.0	0.4 ± 0.1	0.0 ± 0.0
Matrix washed with 10% HNO_3	76.5 ± 2.8	68.6 ± 9.4	81.9 ± 0.0	0.8 ± 0.4	3.8 ± 1.0	3.2 ± 1.0
Metal residue in SFE apparatus						
Flushed with CH_2Cl_2	1.0 ± 0.9	1.3 ± 0.5	0.7 ± 0.7	0.4 ± 0.4	0.6 ± 0.6	0.0 ± 0.0
Flushed with 10% HNO_3	4.5 ± 1.6	11.0 ± 5.1	2.4 ± 0.8	0.7 ± 0.6	2.0 ± 0.3	0.5 ± 0.5
Metal in collection solvent	14.4 ± 1.9	14.3 ± 2.3	8.8 ± 2.3	91.5 ± 8.6	90.1 ± 2.2	97.5 ± 1.8
Total	99.8 ± 0.7	100.8 ± 2.6	95.0 ± 0.5	93.4 ± 8.5	96.9 ± 3.0	101.3 ± 1.4

[a] Recovery of triplicate analysis.

Table 5 Location of radioactive tracer ^{177}Lu(III) after SFE with HFA and TBP

	Per cent recovery^{a}	
Location of analyte	Horizontal extraction cell	Vertical extraction cell
Filter paper	1	1
Extraction cell and fittings	8	< 1
Outlet valve and fittings	6	2
Connection tubing and restrictor	1	1
IBMK collection solvent	78	92
Total	94	97

^{a} Recovery of metal complex in IBMK. Note the recoveries obtained by flushing the apparatus with 50% HNO_3 were < 1% and were therefore not presented in the table. Values are averages of duplicate analyses.

Table 5. The outlet valve is typically situated outside the heated zone (*e.g.*, the oven or tube heater) for ease of operation, but a significant amount (*e.g.*, 6%) of the metal complex was detected in the unheated valve. Conversely, when the valve was situated inside the oven at the same temperature as the extraction cell, only 2% of the complex was detected. It is therefore important that all the extraction apparatus is heated to maintain the solubility of the metal complex throughout the system, with the exception of the restrictor which is placed outside the oven to enable the extract to be collected in the collection solvent.

It was observed that, when CO_2–methanol was used as the extraction fluid, the fused silica restrictor became brittle and fractured. This weakening and fracturing of the silica restrictor has previously been avoided by securing the restrictor inside a stainless steel tube with epoxy resin[35] or by using a commercial stainless steel restrictor. However, in this study, a simple, inexpensive and disposable restrictor was constructed by securing the fused silica capillary inside a PEEK tube with a stainless steel ferrule. With the restrictor now entirely enclosed in PEEK tubing, the CO_2–methanol could be safely depressurised through the restrictor, without breakage, for over 6 h.

Conclusions

To obtain quantitative metal recoveries in an SFE apparatus, a series of conditions must be met, namely: (i) the ligand must be sufficiently soluble and stable to be adequately solvated in the SF; (ii) the metal ion must be efficiently chelated so that charge neutralisation is achieved; (iii) the resulting metal complex must be sufficiently soluble and stable in the SF to be rapidly extracted and effectively swept out of the extraction cell; and (iv) the complex must be quantitatively trapped in the collection device. If the extraction is assessed only on the basis of the collection efficiency data, then the effectiveness of the ligand can be significantly underestimated. Conversely, if only the extraction efficiency data are used in the assessment, then the recovery of the metal could be significantly overestimated. These individual assessments are of limited value as they do not take into account what happens during the transport of the metal complex through the extraction apparatus, namely the potential for metal complex dissociation. Therefore, to fully understand the extraction process, a simple mass balance of the metal before and after the extraction is necessary, and this can be achieved by sequentially flushing the apparatus with solvents to recover any metal residue.

Acknowledgements

The financial support of the Engineering and Physical Sciences Research Council (UK) and BNFL is gratefully acknowledged. Neutron irradiations were performed at Washington State University Nuclear Radiation Centre under a Reactor Sharing Program supported by US DOE.

References

1 Y. Lui, V. Lopez-Avila, M. Alcaraz and W. F. Beckert, *J. High Resolut. Chromatgr.*, 1993, **16**, 106.
2 K. E. Laintz, C. M. Wai, C. R. Yonker and R. D. Smith, *Anal. Chem.*, 1992, **64**, 2875.
3 C. M. Wai, Y. Lin, R. D. Brauer, S. Wang and W. F. Beckert, *Talanta*, 1993, **40**, 1325.
4 J. Wang and W. D. Marshall, *Anal. Chem.*, 1994, **66**, 3900.
5 Y. Liu, V. Lopez-Avila, M. Alcaraz, W. F. Beckert and E. M. Heithmar, *J. Chromatogr. Sci.*, 1993, **31**, 310.
6 Y. Lin, R. D. Brauer, K. E. Laintz and C. M. Wai, *Anal. Chem*, 1993, **65**, 2549.
7 Y. Lin, C. M. Wai, F. M. Jean and R. D. Brauer, *Environ. Sci. Technol.*, 1994, **28**, 1190.
8 K. E. Laintz and E. Tachikawa, *Anal. Chem.*, 1994, **66**, 2190.
9 S. Wang, S. Elshani, and C. M. Wai, *Anal. Chem.*, 1995, **67**, 919.
10 J. Dachs, R. Alzaga and M. Bayona, *Anal. Chim. Acta*, 1994, **286**, 319.
11 M. Johansson, T. Berglöf, D. C. Baxter and W. Frech, *Analyst*, 1995, **120**, 755.
12 S. L. Cleland, L. K. Olson, J. A. Caruso and J. M. Carey, *J. Anal. At. Spectrom.*, 1994 **9**, 975.
13 J. Wang and W. D. Marshall, *Analyst*, 1995, **120**, 623.
14 K. G. Furton, L. Chen and R. Jaffè, *Anal. Chim. Acta*, 1995, **304**, 203.
15 J. Wang and W. D. Marshall, *Anal. Chem.*, 1994, **66**, 1658.
16 M. Ashraf-Khorassani, R. H. Houck and J. M. Levy, *J. High Resolut. Chromatogr.*, 1992, **30**, 361.
17 M. D. Burford, S. B. Hawthorne, D. J. Miller and T. Braggins, *J. Chromatogr.*, 1992, **609**, 321.
18 K. E. Laintz, J.-J. Yu and C. M. Wai, *Anal. Chem.*, 1992, **64**, 311.
19 K. Jinno, H. Mae and C. Fujimoto, *J. High Resolut. Chromatogr.*, 1990, **13**, 13.
20 M. Ashraf-Khoassani, J. W. Hellgeth and L. T. Taylor, *Anal. Chem.*, 1987, **59**, 2077.
21 M. D. Burford, A. A. Clifford, K. D. Bartle, C. M. Cowey and N. G. Smart, *J. Chromatogr.*, 1996, **738**, 241.
22 R. M'Hamdi, J. F. Bocquet, K. Chhor and C. Pommier, *J. Supercritical Fluids*, 1991, **4**, 55.
23 A. Tavlaridis and R. Neeb, *Fresenius' Z. Anal. Chem.*, 1978, **242**, 135.
24 N. Saito, Y. Ikushima and T. Goto, *Bull. Chem. Soc. Jpn.*, 1990, **63**, 1532.
25 N. G. Smart, T. Carleson, T. Kast, A. A. Clifford, M. D. Burford and C. H. Wai, *Talanta*, 1997, **44,** 137.
26 Z. B. Alfassi and C. M. Wao, *Preconcentration Techniques for Trace Elements*, CRC Press, Boca Raton, Ann Arbor, London, 1992.
27 S. R. Hutchins, P. R. Haddad and S. Dilli, *Chrom.*, 1982, **251**(15), 185.
28 K. E. Laintz, C. M. Wai, C. R. Yonker and R. D. Smith, *J. Supercritical Fluids*, 1991, **4**, 194.
29 P. C. Uden, *J. Chromatogr.*, 1994, **313**, 3.
30 E. W. Berg and H. W. Dowling, *J. Chem. Eng. Data*, 1961, **6**, 556.
31 R. C. Mehrotra, R. Bohra and D. P. Gaur, *Metal ß-Diketonates and Allied Derivatives*, Academic Press, London, 1978, p. 59.
32 J. Noro and T. Sekine, *Bull. Chem. Soc. Jpn.*, 1993, **66**, 1647.
33 K. L. Toews, R. M. Shroll, C. M. Wai and N. G. Smart, *Anal. Chem.*, 1995, **67**, 4040.
34 S. B. Hawthorne, D. J. Miller, M. D. Burford, J. J. Langenfeld, S. Eckert-Tilotta and P. K. Louie, *J. Chromatogr.*, 1993, **642**, 301.
35 M. D. Burford, S. B. Hawthorne, D. J. Miller and J. Macomber, *J. Chromatogr.*, 1993, **648**, 445.

Paper 8/09021A