

New fluorinated hydroxamic acid reagents for the extraction of metal ions with supercritical CO₂

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Abstract

Research to date on the supercritical fluid extraction (SFE) of metal ions has focused on the use of dithiocarbamates and β -diketones. Hydroxamic acids are well known as effective chelating agents for a broad range of transition metal ions. Much attention has centred in inorganic chemistry on the effect of N-substitution on metal chelate stability and selectivity, and in analytical chemistry on the immobilisation of the chelating agents to the chosen solid supports such as silica. In this paper, the synthesis of selected fluorinated mono hydroxamic acids and their N-substituted derivatives is reported. The new reagents are applied in the SFE of metal ions in particular Fe(III) using unmodified supercritical CO₂. Metal extraction is monitored using atomic absorption spectroscopy and visible spectrophotometry. The extraction efficiencies were determined as a function of pressure and temperature. The new ligands synthesised and applied were perfluorooctanohydroxamic acid (PFOHA), heptafluorobutyrylhydroxamic acid (HFBHA) and their N-methylhydroxamic acid derivatives. Of the synthesised reagents, PFOHA was the most soluble and effective extractant of Fe(III) from spiked filter paper, reaching 97% extraction of the metal ion under optimised conditions. The selectivity of this ligand for Fe(III) in the presence of Cu(II), Ni(II), Pb(II) and Zn(II) is also demonstrated.

Keywords: Extraction methods; Complexation; Supercritical fluid; Metal cations; Hydroxamic acids

1. Introduction

Supercritical fluid extraction (SFE) has become a viable alternative to conventional solvent extraction for the recovery of organic compounds from environmental and biological samples. It has several advantages, including increased speed, better recovery and the reduction in both solvent usage and solvent waste generation. To date, most of the published work has concentrated on the extraction of organic compounds. Extraction of free metal ions by supercritical carbon dioxide (SF-CO₂) is known to be highly inefficient due to the polar nature of the

metal ion and the non-polar nature of the supercritical fluid. Charge neutralisation of the metal ion is required before it can be extracted by SF-CO₂. This can be achieved by binding the metal ions to organic ligands resulting in neutral complexes, with improved solubilities in SF-CO₂. Interestingly, some of the earliest supercritical fluid work involved nickel porphyrin complexes [1]. Since then several studies have been reported on the separation [2–4] and spectroscopic behaviour [3] of metal chelates in supercritical fluids. Metal chelates of dithiocarbamates [5,6] have shown good separation in supercritical fluid chromatography. Laintz et al. have shown that a number of metal dithiocarbamates have limited solubility in supercritical fluids [7]. However, these

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solubilities were enhanced by several orders of magnitude by substituting fluorine for hydrogen in the ligand [4,8]. Mercuric ions (Hg^{2+}) were extracted from solid samples [9] (cellulose matrix) using methanol modified SF- CO_2 containing the fluorinated chelating agent lithium bis(trifluoroethyl)-dithiocarbamate. Fluorination was extended to the β -diketones where a fluorinated β -diketone in conjunction with tributyl phosphate, extracted thorium and uranium ions from solid and liquid materials [10]. Saito et al. [11] found that acetylacetonate (acac) chelates were successfully extracted with SF- CO_2 with selectivity for $\text{In}(\text{acac})_3$ in the presence of other bis(acetylacetonate) chelates. Over recent years several studies have been carried out to investigate the use of SFE for extracting organotin compounds from environmental samples [12–15]. These studies have successfully applied approaches involving in situ derivatisation using hexylmagnesium bromide [14] and complexation with dithiocarbamate [15] to provide SFE extracts for subsequent gas chromatographic analysis. Yazdi et al. [16] have designed a number of highly SF- CO_2 soluble chelating agents, by chemically incorporating a highly CO_2 -philic fluorinated polyether tail.

Hydroxamic acids have been used as reagents in analytical chemistry for gravimetric, spectrophotometric, flow-injection analysis [17] and solid-phase extraction of metal ions [18,19]. In the earlier years, hydroxamic acids were used as reagents for the colorimetric determination of metals [20,21]. Characteristic coloured chelate compounds with metal ions such as Fe(III), $\text{UO}_2(\text{II})$, Ti(IV), V(V) and Cu(II) have been formed [22]. Applications of the reagents in the chromatographic analysis of metal ions have also been made. On-line trace metal ion preconcentration in ion chromatography using hydroxamate dextran-coated silicas has been reported by this laboratory [23]. Palmieri and Fritz [24] chromatographically separated Zr(IV), Hf(IV), Fe(III), Nb(V), Al(III) and Sb(III) on a reversed-phase polymeric column using a synthetic water soluble complexing agent, N-methylfluorohydroxamic acid.

The present work reports the synthesis of fluorinated aliphatic hydroxamic acids and the SFE of Fe(III) and other metal ions from cellulose-based material using these newly synthesised reagents is demonstrated. The solubility of these ligands in SF-

CO_2 is also measured, including the effects of chain length and N-methyl substitution on extraction efficiency.

2. Experimental

2.1. Reagents

The esters, methyl perfluorooctanoate and methyl heptafluorobutyrate were purchased from Fluorochem (Derbyshire, UK) while hydroxylammonium chloride was obtained from BDH (Poole, UK) and N-methylhydroxylamine hydrochloride was purchased from Aldrich (Dorset, UK). $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (BDH) was the metal salt used for the extraction experiments of Fe(III) from cellulose material.

2.2. Synthesis of fluorinated hydroxamic acids

To a cooled solution of 30 ml methanol containing equimolar amounts of the fluorinated ester (0.0037 mol) and hydroxylammonium chloride (or N-methylhydroxylamine hydrochloride) was added 10% excess KOH (0.00407 mol). After 5 h mixing at -5°C , the reaction mixture was left to stir at room temperature for a further 5 days. All volatiles were then removed to leave the very crude hydroxamic acid product.

For the purification of perfluorooctanohydroxamic acid (PFOHA), 100 ml of 5% aqueous acetic acid was added to the colourless solid. The contents were left to stir for 3 h after which the solution was filtered and washed with 150 ml of deionised water to leave the purified hydroxamic acid (83% yield). Theory: C=22.37%, H=0.47%, N=3.26%; found: C=22.24%, H=0.76%, N=3.47%. Infrared analysis showed a strong absorption at $\nu=1690\text{ cm}^{-1}$ (C=O), characteristic of the C=O stretch of hydroxamic acids.

N-Methylheptafluorobutyrylhydroxamic acid (MHFBHA), heptafluorobutyrylhydroxamic acid (HFBHA) and MPFOHA proved more difficult to isolate in a pure form using established approaches. Small amounts of pure solid were, however, obtained by SFE. 100 mg of the crude hydroxamic acid product was statically extracted for 20 min followed by 15 min dynamic extraction at 70°C and 300 atm

into a collection solvent of 8 ml of methanol (1 atm=101 325 Pa). The methanol was evaporated to leave the purified hydroxamic acid reagent. For example, the CHN results determined for MPFOHA before and after SFE were as follows: MPFOHA; theory: C=24.38%, H=0.903%, N=3.16%; found before SFE: C=19.60%, H=1.40%, N=3.48%; found after SFE: C=24.73%, H=1.14%, N=3.3%. $\nu=1667\text{ cm}^{-1}$ (C=O). All these reagents gave the positive result on spot testing with Fe(III).

2.3. Instrumentation

2.3.1. Supercritical fluid extraction

All extractions were performed using an Isco SFX SFE system (Isco, USA, supplied by Jones Chromatography, UK). The SFE system was controlled by a 260D Series Pump controller, allowing programming of pressure automatic refill and continuous flow. It consisted of a syringe pump, heated extractor block and restrictor. Ligand reagents and metal loaded phases were loaded into an open ended glass tube (3.0×0.5 cm I.D.), packed with glass wool at both ends and mounted inside a stainless steel cartridge (5.5×0.76 cm I.D., volume 2.5 ml). Extracted samples were collected in a liquid-trap containing methanol (Merck, Germany). A variable heated restrictor, set at a temperature 5°C below the oven temperature was used in these studies. Pressure was varied in the range 200 to 400 atm and the temperature of the extractor was set between 60 and 120°C. SFE extracts were analysed using both UV-visible spectrophotometry and atomic absorption spectroscopy (AAS). The carbon dioxide cylinder with dip tube was obtained from Irish Oxygen (Cork, Ireland) and was used without the addition of a modifier.

2.3.2. Solubility measurements

An empty glass tube (3.0×0.5 cm I.D.) was inserted into a stainless steel extraction vessel (volume 2.5 ml) reducing the volume of the extraction chamber to 2.2 ml. Hydroxamic acid samples (ca. 80 mg) were loaded into the glass tube to avoid any possibility that loose reagent particles would make their way towards the stainless steel frit at the exit of the extraction cell. The glass tube was plugged with glass wool at both ends of the tube, weighed and inserted into the stainless steel vessel which was

tightened into the heating block and statically extracted for 30 min at 200 atm and 60°C. The extraction cell was then vented into a collection vessel containing 5 ml of methanol by opening a valve between the extraction vessel and the collecting solvent. The methanol was rotatory evaporated and the mass of the ligand collected corresponded to the amount extracted by 2.2 ml CO₂.

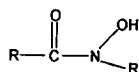
2.3.3. Supercritical fluid extraction of Fe(III)

For the metal extraction experiments, 130 μl of Fe(III) nitrate solution in methanol [0.13 μg of Fe(III)] was spiked onto filter paper (3×1 cm). Similarly, for the extraction studies in the presence of other metal ions 40 μl of 1000 ppm stock solutions (Merck) of Fe(III), Mn(II), Pb(II), Ni(II) and Cu(II) were spiked onto filter paper (3×1 cm). The filter paper was allowed to dry and where indicated, was then spiked with 40 μl deionised water. The filter paper along with 30 mg of the fluorinated hydroxamic acid (or the N-methyl derivative) was loaded into a glass tube (3×0.5 cm I.D.), plugged with glass wool at both ends and also between the filter paper and the hydroxamic acid sample. The glass tube was mounted inside a stainless steel extraction vessel, tightened into the heating block and statically extracted using unmodified SF-CO₂ for 20 min at 300 atm at applied temperatures between 60 to 120°C. The extraction cell was vented into a collection vessel containing 8 ml of methanol (dynamic extraction). Having established the optimum temperature for each ligand, the pressure was varied between 200 to 400 atm. Collected extracts were analysed by AAS and visible spectrophotometry. The % extraction was determined by direct comparison with collecting solutions spiked with standard Fe(III) solution. Finally, the extraction was studied as a function of added ligand under optimum extraction conditions, in the presence of added water and of other metal ions.

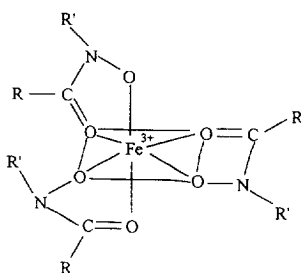
3. Results

The fluorination of selective ligands has been shown to enhance their solubilities in SF-CO₂ [4,8]. The fluorinated aliphatic ligands synthesised in this

work are shown in Fig. 1, together with the structure of a typical octahedral hydroxamate complex. These complexes have the necessary attributes of neutrality and high stability. Initial experiments were performed to determine the optimum conditions for the SFE of Fe(III) from spiked filter paper using these newly synthesised fluorinated hydroxamic acids and unmodified SF-CO₂. Using a pressure of 300 atm and analysing the collected extracts for Fe(III) by AAS, the temperature was varied between 60 and 120°C and the optimum temperatures found were 70°C for the longer chained PFOHA and MPFOHA and 80°C for the shorter chain MHFBHA and HFBHA ligands. At these set optimum temperatures, subsequent variation of the applied pressure between



REAGENT:	R:	R':
PFOHA	CF ₃ (CF ₂) ₆	H
HFBHA	CF ₃ (CF ₂) ₂	H
MPFOHA	CF ₃ (CF ₂) ₆	CH ₃
MHFBHA	CF ₃ (CF ₂) ₂	CH ₃



Fe(RCONOHR')₃

Fig. 1. Chemical structures of the fluorinated aliphatic hydroxamic acids and a typical Fe(III)–hydroxamate complex formed during SFE.

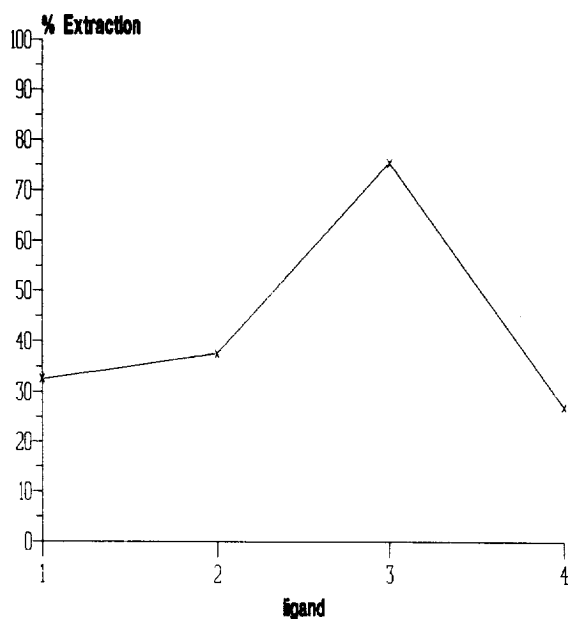


Fig. 2. % Extraction of Fe(III) from filter paper for four selected hydroxamate reagents (30 mg each, 40 μ l added water), 1: MHFBHA; 2: HFBHA; 3: PFOHA; 4: MPFOHA.

200 to 400 atm revealed that 300 atm was indeed the optimum pressure for extraction. Fig. 2 shows the % extraction of Fe(III) obtained using 30 mg of each ligand and 40 μ l of added water at these optimum conditions. N-Methyl substitution is known to increase the stability of hydroxamic acid complexes [25], but surprisingly the N-methylhydroxamic acids extracted less Fe(III) from the filter paper than their unsubstituted analogues. Another noticeable feature from Fig. 2 is the difference in the extraction efficiency between the shorter and longer chained hydroxamic acids; PFOHA shows a % extraction of 76% while HFBHA extracts only 39% Fe(III) using equivalent masses of ligand. In the absence of these ligands, no Fe(III) is extracted from filter paper.

The solubilities of the fluorinated aliphatic hydroxamic acids were determined using the method previously described [9]. The solubilities are given in terms of mmol of sample in a litre of CO₂. Solubilities of 29.9 mmol l⁻¹, 44.0 mmol l⁻¹ and 36.5 mmol l⁻¹, were determined for MHFBHA, HFBHA and MPFOHA, respectively at 200 atm and 60°C, while PFOHA showed a much higher solubility of >77.9 mmol l⁻¹ under these same operating con-

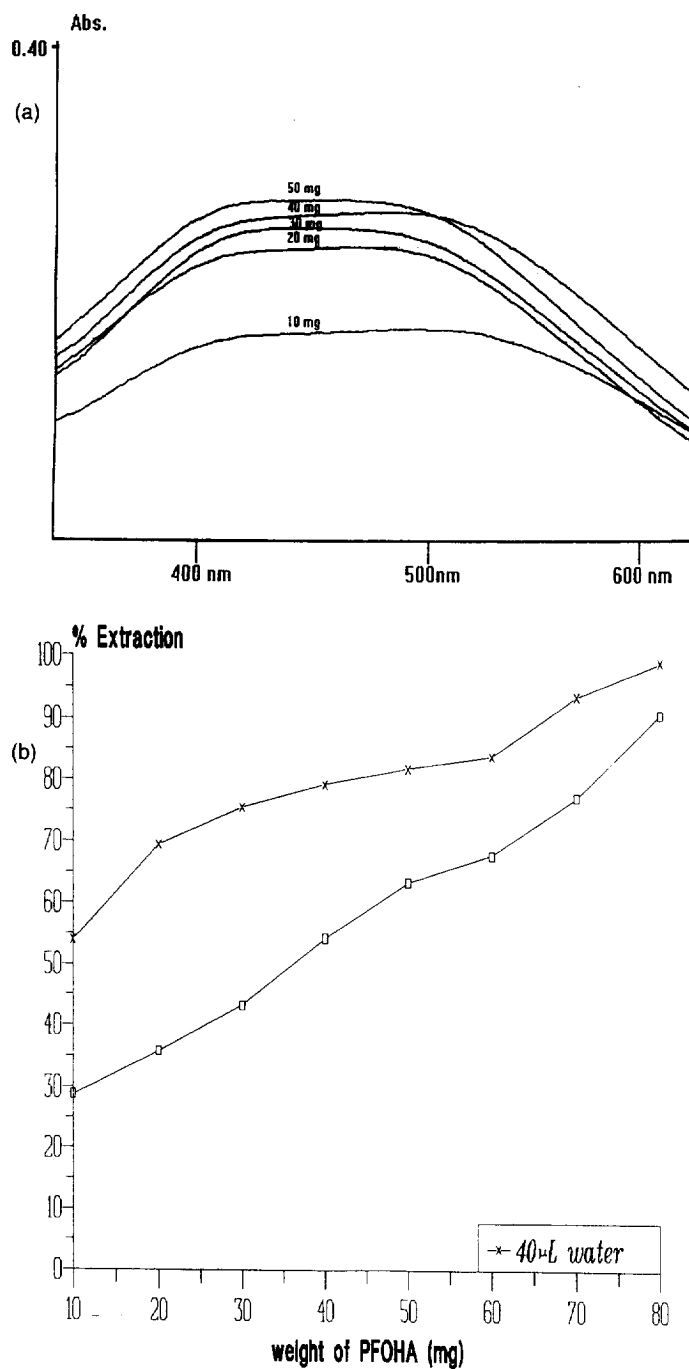


Fig. 3. SFE of Fe(III) using increasing amounts of PFOHA in the presence and absence of water. (a) Visible absorbance spectra of the resulting Fe(III)-hydroxamate complex collected after SFE (300 atm, 70°C, 40 µl water, 20 min static, 10 min dynamic). (b) Corresponding plots of % extraction versus mass of reagent, as determined by AAS.

ditions. These results parallel findings of enhanced solubilities of other fluorinated ligands and complexes such as the fluorinated β -diketone complexes [26]. Yazdi et al. [27] have recently synthesised several novel, highly CO_2 -soluble chelating agents that exhibit solubilities in excess of 100 mmol l^{-1} of CO_2 . The N-methyl derivatives showed lower solubility and thus lower extraction efficiency due to the extra non-fluorinated methyl group. Further optimisation studies involved the variation of the amount of ligand (10 mg to 80 mg) while keeping the amount of Fe(III) constant. The ligand chosen was PFOHA since it gave the highest extraction efficiencies. Two separate studies were investigated: one involving the addition of $40 \mu\text{l}$ of water to the filter paper and the second without added water. Under the same conditions, the SFE extractions carried out with added water yielded higher extraction efficiencies for Fe(III). Previously, Wai et al. have shown that the extraction of metal ions from cellulose-based matrix is enhanced with the addition of water which acts as a matrix modifier [9]. In this work, which describes the first results of metal extraction using fluorinated hydroxamic acids, the positive effect of added water is also reported. Fig. 3a shows the characteristic visible absorbance band for Fe(III)–hydroxamate binding at the different concentrations of ligand added (10 mg to 50 mg) in the presence of added water. This characteristic visible absorption band increases at higher concentrations of ligand indicating higher amounts of the Fe(III)–hydroxamate complex being formed and extracted. Fig. 3b shows the corresponding % extraction values (determined from AAS analysis) versus amount of ligand added, with and without $40 \mu\text{l}$ of water spiked onto the filter paper. These results show that up to 97% Fe(III) can be extracted from the filter paper using 80 mg of ligand and $40 \mu\text{l}$ of water. Furthermore, in the presence of a metal mixture containing Mn(II), Pb(II), Ni(II) and Cu(II), PFOHA displayed selective extraction of 86% Fe(III), with Cu(II) extraction of 9.5% and the extraction efficiencies not greater than 5% recorded for the other transition metals. Preliminary experiments involving the SFE of Fe(III) from metal loaded peat samples have shown that PFOHA is an efficient ligand for this extraction procedure.

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