(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
11 September 2009 (11.09.2009)

PCT

(10) International Publication Number
WO 2009/109754 A1

(51) International Patent Classification:
B01D 11/02 (2006.01) *G21F 9/28* (2006.01)
C22B 3/00 (2006.01) *C11D 11/00* (2006.01)
B08B 7/00 (2006.01) *D06F 43/00* (2006.01)
B09C 1/02 (2006.01)

(21) International Application Number:
PCT/GB2009/000602

(22) International Filing Date:
4 March 2009 (04.03.2009)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
0804055.2 4 March 2008 (04.03.2008) GB

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(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

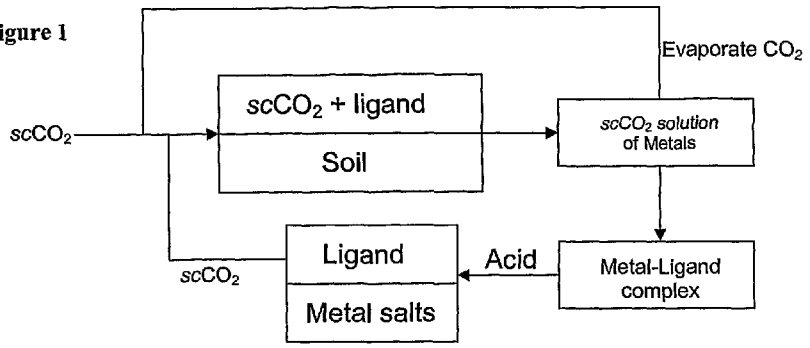
Published:

— *with international search report (Art. 21(3))*

WO 2009/109754 A1

(54) Title: CLEANING METHOD

Figure 1



(57) Abstract: The application relates to a method for extracting a metal comprising: exposing a metal containing material to (i) liquid solvent or supercritical solvent; in combination with (ii) a perfluorinated phosphine. Perfluorinated phosphines are also provided.

Cleaning Method

The invention relates to methods for extracting metals, for example metal contaminants, comprising the use of a liquid solvent or supercritical solvent, in combination with a perfluorinated phosphine. The invention also relates to the combination of a supercritical solvent with a perfluorinated phosphine, and to novel and inventive perfluorinated phosphines.

The contamination of the environment by toxic metals is a major problem that can require expensive clean-up procedures. This work aims to develop *ex-situ* soil cleanup for a number of toxic metals. These can be broadly classed as actinide elements and heavy metal waste from industry and mining applications. Thus, the release of actinide elements into the environment is a major public health concern, and has come sharply into focus with the UK government's recent commitment to nuclear power and the use of depleted uranium munitions in recent conflicts in the Balkans and Gulf regions. Given the toxicity of these metals, it is of obvious importance to remove them from the environment before they get into the food chain, otherwise serious health problems from acute radiation damage, chemical toxicity and late radiation effects will result. As an example, the ingestion of plutonium has been shown to increase the chances of bone tumours, as the ions are effectively immobilised on the surface of the bone.[1] Many studies have show that the bioavailability of actinide ions is greater than first suggested thus allowing these ions to cross physiological barriers leading to a concentration in the food chain. In this regard, plutonium migration is of particular concern as it has similar physical properties to iron, and examples exist of bacteria effectively sequestering plutonium allowing a further method of food chain contamination.[2] Additionally, the Nuclear Decommissioning Agency has recently announced a review of contaminated land at 20 of the nuclear reactors in the UK.[3] There is also a timely relevance considering the proposals of waste nuclear fuel deposition in underground repositories – the UK's inventory of ca. 100 tonnes of plutonium has been recommended for being stored in such repositories.[4] Given the substantial scientific and technological challenges towards the safe deposition of highly radioactive materials for millions of years, there is a danger that soil contamination could occur via leakage or rupture of the storage materials. Thus there

is a need to improve the performance of known re-mediation techniques for radioactive waste management.

Heavy metal contamination is a more conventional problem faced by many areas of the UK, especially those that have been heavily industrialised in the past but where these industries have moved on or closed down. For example, production of household batteries has left a serious contamination issue of toxic metals such as mercury, cadmium and lead for brown field sites across the UK, which hampers regeneration of the land.[5] Indeed, in a recent survey of soil by the Environment Agency the mean concentration of cadmium in industrial herbage was more than three times that found in urban or rural herbage[6] – this can constitute a pathway into the food chain. A further concern for potential cadmium contamination is that mobile phone batteries contain cadmium, and there are ca. 15 million mobile phones discarded every year into landfill sites in the UK, although new WEEE regulations will probably reduce this risk.[7] Chromium contamination is another area of concern and this can arise from such diverse manufacturing processes as the production of photocopy machines to chrome-plating to textile dyes. In the United States, chromium is present in two thirds of the 1,591 sites that are on the National Cleanup Priority list (as of 2001).[8]

Currently one of the main techniques for dealing with large scale contamination is to remove the soil to a depth that includes all contaminants and transferring this to a landfill site. However this method is no longer viable as new landfill regulations severely restrict the materials that can be buried;[9] indeed mercury, cadmium, chromium, lead, arsenic, uranium and thorium are amongst those metals covered in associated legislation pertaining to groundwater contamination from landfill sites.[10] Soil washing is an option but this relies on the use of organic solvents to extract the metal contaminants from the soil. These are typically time and labour intensive and, due to tighter controls on solvent disposal, becoming increasingly more expensive.[11] One recent suggestion has been in the use of supercritical CO_2 ($scCO_2$) as it could reduce the amount of organic wastes.[12] $scCO_2$ is an excellent choice for a solvent as it is non flammable, non toxic and is a renewable feedstock of low cost. These properties have led to a number of uses within the academic and industrial communities and have been described as a "green" or environmentally benign solvent.

The extraction of metals using a supercritical solvent such as carbon dioxide is generally known in the art. See for example US 5,356,538, US 5,770,085, US 6,132,491, US 6,187,911 and WO2006/023779.

Such prior processes have utilised, for example, trialkyl phosphate, triaryl phosphate, trialkylphosphine oxide, triarylphosphine oxide, beta-diketones to chelate metal contaminants.

The inventors have now identified an alternative series of chelators having improved properties. For example, a number of the chelators have selectivity for heavy metals, allowing heavy metals to be selectively removed. This means that problem contaminants, such as mercury, may be selectively removed from, for example soil, whilst still leaving useful metals, such as calcium or magnesium, in the soil.

JP 2000087013 discloses phosphate ester containing water and oil repellent compositions utilising a perfluorinated phosphine oxide. JP 11343416 similarly discloses perfluoroalkyl phosphate ester salts, which are used to treat silicone resin powders in the production of cosmetics. Perfluorinated alkyl phosphates have also been used to disperse metallic metal powder in magnetic paint (JP 62250937).

The invention provides a method for extracting a metal comprising exposing a metal-containing material to (i) a liquid solvent or supercritical solvent, in combination with (ii) a perfluorinated phosphine. The perfluorinated phosphine acts as a chelator and binds to one or more metals within the material to remove it from the material.

The phosphine is particularly useful for use in combination with a supercritical solvent, such as carbon dioxide. Supercritical solvents are solvents that are at temperatures and pressures beyond their critical points. For example, the critical pressure of a substance is the highest pressure at which the substance can exist as a true liquid, no matter what the temperature. However, some gases at supercritical conditions are nearly as dense as some liquids due to the extreme temperature and pressure. This makes these gases ideal as solvents. Carbon dioxide is especially useful as a supercritical fluid. The reason for the popularity of carbon dioxide is that

it has critical points as low as approximately 31°C and 74 bar. However, other solvents, including other supercritical solvents could also be used. For example, water can also act as a supercritical solvent, though at much higher temperatures (37.4°C and 222.3 bar). Other supercritical solvents include xenon and ethane.

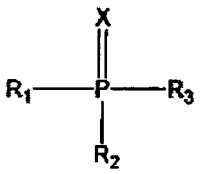
The phosphine may also be useful with more conventional organic and inorganic solvents, such as water or alcohols. Organohalides, for example alkyl halides and alkyl furans, such as chloro- or fluoro-forms may also be used. Preferred solvents include dichloromethane, and perfluorinated organohalide solvents, such as perfluorohexane, perfluorocyclohexane, perfluoro(butyltetrahydrofuran) or perfluoro-methylcyclohexane. Liquid (sub-critical) CO_2 may also be used. Such solvents are generally known in the art

Perfluorinated solvents have many similar properties to many supercritical solvents such as $scCO_2$. For example they have low polarity compared to many solvents such as water or ionic liquids . They also have relatively high volatility compared to many solvents. See for example Clark J.H & Tavener S.T. Org. Process. Res. Dev (2007), Vol 11, 149-155. Phosphine complexes have been previously demonstrated have similar solubility in fluorous and $scCO_2$ solvents (Stribany R.T. and Gorun S.M. J Organometal. Chem. (1999), Vol 579, 217-221.

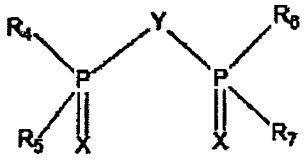
However, supercritical solvents are especially useful because they can be readily removed from the phosphine (for example when bound to metal), via evaporation. The evaporated supercritical solvent can then be recycled for re-use.

Preferably the perfluorinated phosphine is a perfluorinated phosphine oxide or perfluorinated phosphine sulphide.

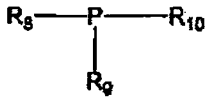
Most preferably, the perfluorinated phosphine has a general formula: I, II or III;



I



II



III

where:

each of groups R1, R2, R3, R4, R5, R6, R7, R8, R9 and R10, are independently selectable and are branched, straight or cyclic fluorocarbon groups, optionally comprising one or more alkyl moieties, preferably having the general formula $CF_3(CF_2)_n(CH_2)_m$, wherein one or more adjacent groups may be joined to form one or more rings where;

m is preferably 1, 2, 3, 4, 5, 6, 7, 8, 9 or 10. Most preferably m may be 2 or 3.

n maybe any integer from 0-20, but is most preferably 3, 5, 7, 9 or 11, or 7 or less, or 5 or less.

Preferably, each of R1, R3 and R2; R4, R5, R6 and R7; and R8, R9 and R10 are the same.

Two or more adjacent groups may form a ring, such as C_6F_{11} or two fused rings, such as C_9F_{17}.

X is preferably oxygen or sulphur, most preferably oxygen.

The compound may have a formula I

The compound may have a formula II, where n is 7 or less and X is O

However phosphine sulphides, (for example those shown in equation 5 below) have been found to be especially selective for the extraction of mercury and cadmium.

Y may be any suitable linker group. However it is preferably an alkyl, especially a straight chain alkyl. Preferably the alkyl contains between 1 and 6 carbon atoms, most preferably 2 carbon atoms.

The method may also comprise exposing the metal containing material to an oxidising agent, such as a mineral acid or nitric acid. Exposing the material to an oxidising agent may help to release contaminating metal from the material.

Preferably the metal containing material is selected from soil or other contaminated material. It also includes laboratory waste, such as clothing or other waste, and includes the cleansing of laboratory utensils such as laboratory equipment and surfaces.

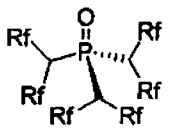
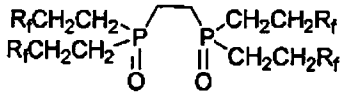
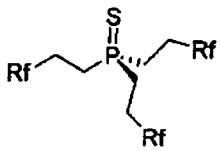
Preferably the metal is selected from one or more of cadmium, strontium, plutonium, uranium, lead, mercury, chromium, arsenic, antimony, tellurium, polonium, germanium and salts thereof.

The method preferably includes separating the solvent from the perfluorinated phosphine and recycling the solvent.

The metal-perfluorinated phosphine complex left may then be cleaned, for example by the treatment with an acid, to leave cleaned perfluorinated phosphine for re-use, and recovered metal, for example in the form of a metal salt. Metal salt may then be disposed of or re-used for other purposes.

A second aspect of the invention also provides the combination of (i) a supercritical solvent and (ii) a perfluorinated phosphine. The perfluorinated phosphine and/or the supercritical solvent, is preferably as defined according to any of the first aspect of the invention. The combination is preferably coordinated to a metal selected from one or more of cadmium, strontium, plutonium, uranium, lead, mercury chromium, arsenic, antimony, tellurium, polonium, germanium and salts thereof.

Further aspect of the invention provides a perfluorinated phosphine selected from:

$(Rf(CH_2)_y)_3P$   

Where $Rf = CF_3(CF_2)_n$

n = an integer of 1-20

y = 3 or 4

Preferably the perfluorinated phosphine is utilised in the method according to the first aspect of the invention or is used in combination with the supercritical solvent according to the second aspect of the invention.

A summary of a preferred method of the invention is shown in Figure 1.

Figure 2 shows a summary of the different methods that may be used to produce examples of the phosphine ligands that may be used in the invention.

The reaction schemes (1) and (2) shown in, for example, the literature (14, 15), JP 2000087013, JP 11343416 and JP 62250937.

Rf refers to a perfluorine group, such as $CF_3(CF_2)_n$, where n is an integer of 1-20, for example as defined above.

Figures 3 and 4 show the results of reactions for the compound $[CF_3(CF_2)_5CH_2CH_2]_3P=O$.

Figure 3 shows (a) UV/vis spectra of the compound, uranyl acetate and the uranyl complex; (b) IR spectrum of the ligand and the uranyl complex.

Figure 4 shows that plot of the absorbance at 352nm vs ligand concentration.

Figure 5 shows ^{31}P NMR spectra of (a) lead nitrate (b) $Bu_2Sn(OMe)_2$ in CD_3OD.

Metal binding studies

Perfluorohexane solvent (FC72)

Data

The ligands $\{CF_3(CF_2)_nCH_2CH_2\}_3P{=}O$ and $\{CF_3(CF_2)_nCH_2CH_2\}_3P$ were prepared via the literature method (G. Vlád, F.U. Richter and I.T. Horváth, *Tetrahedron Lett.*, 2005 **46** 8605.) The radioisotopes $^{90}Sr(NO_3)_2$ and $^{133}Ba(NO_3)_2$ were purchased from Amersham International, Uranyl Nitrate from BDH and $^{59}FeCl_3$ from Perkin Elmer. FC-72 was obtained from Acota and distilled before use. All other materials were obtained from Aldrich and used as received. NMR spectra were recorded on a JEOL ECX-400 at 399.7 MHz (^1H), 376.1 MHz (^{19}F), 161.8 MHz (^{31}P) and 100.50 MHz (^{13}C). Infrared spectra were recorded on a Perkin Elmer Spectrum 100 with ATR. UV-vis spectra were recorded on a Perkin Elmer Lambda 25 spectrometer. DSC spectra were recorded on a Perkin Elmer Diamond DSC. ICP-OES measurements were recorded on a Perkin Elmer Optima 2100 DV spectrometer; calibration standards were purchased from Acros Organics and used as received. Gamma analysis was performed on a Canberra Packard Cobra Auto-Gamma well type gamma counter. Count time was 5 minutes per sample which gave the lowest error in the measurement. ^{90}Sr and uranium measurements were performed on a Canberra Packard Tricarb 2250CA scintillation counter (in the low-level alpha mode for uranium). Count times were 1 minute per sample which gave acceptable errors (2σ = 1-5%).The errors introduced by the sampling of the phases and other volumetric operations are typically ± 3%. Cumulative error including the counting error leads to an experimental average error uniformly taken to be ± 5%.

Synthesis of $\{CF_3(CF_2)_5CH_2CH_2\}_3P{=}S$. To a solution of $\{CF_3(CF_2)_5CH_2CH_2\}_3P$ (1 mmol) in CH_2Cl_2 (20 cm^3) was added excess sulphur and the resulting solution refluxed under a nitrogen atmosphere for 1 hour. The solvent was removed *in vacuo* and the residue extracted with FC-72 (3 x 10 cm^3). Removal of the solvent afforded a white microcrystalline solid (94%). MPt: 85.2 °C; ^1H NMR (d-acetone): 2.49 (m, 6H, CH_2) 2.71 (m, 6H, CH_2); ^{19}F NMR (d-acetone): -82.6 (t, $^2J_{FF}$ = 15 Hz, CF_3), -103.4 (m CF_2CH_2), -118.1 (CF_2), -118.9 (CF_2), -120.1 (CF_2), -121.8 (CF_2); ^{31}P NMR (d-acetone): 52.5 (s); ms (EI):1103.7 [30%, M^+], 1084.7 [100%, M-F^+], 757.9 [70%, M-R_f^+], 412.0 [40% M-Rf_2^+].

Synthesis of $(R_f)_2P(O)CH_2CH_2P(O)(R_f)_2$. To solid $(R_f)_2PCH_2CH_2P(R_f)_2$ was added 2.5 equivalents of H_2O_2 (30 wt% solution in water). The mixture was stirred for 3 hours and then the excess peroxide decomposed by heating to 90 °C until all the water had been evaporated. The residue was extracted into 1,4-Bis(trifluoromethyl) benzene and dried over $MgSO_4$. Removal of the solvent afforded a white microcrystalline powder.

Rf = $CF_3(CF_2)_5CH_2CH_2$; Yield 78%; MPt: 134-138 °C; ^1H NMR (FC-72): 1.08 (m, 6H, CH_2) 1.29 (m, 6H, CH_2), 3.14 (m, 4H, CH_2CH_2); ^{19}F NMR (FC-72): -84.5 (t, $^2J_{FF}$ = 15 Hz, CF_3), -103.1 (m CF_2CH_2), -118.7 (CF_2), -119.2 (CF_2), -120.9 (CF_2), -122.5 (CF_2); ^{31}P NMR (d-acetone): 31.6 (s). ms (EI):1511.7 [40%, M^+].

Rf = $CF_3(CF_2)_9CH_2CH_2$; Yield 45%; MPt: 162-168 °C; ^1H NMR (FC-72): 1.10 (m, 6H, CH_2) 1.32 (m, 6H, CH_2), 3.18 (m, 4H, CH_2CH_2); ^{19}F NMR (FC-72): -84.7 (t, $^2J_{FF}$ = 14 Hz, CF_3), -102.7 (m CF_2CH_2), -118.4 (CF_2), -119.1 (CF_2), -120.7 (CF_2), -122.5 (CF_2); ^{31}P NMR (d-acetone): 32.8 (s).

Solution Extraction Studies.

In order to determine distribution ratios (D = $[M]_{org}/[M]_{aq}$) of the metals and metalloids of interest, the metal solutions (1 cm^3 of a 20ppm stock solution) was placed in a sample vial and made up to 5 cm^3 with distilled water. The required amount of extractant was dissolved in 5 cm^3 of FC-72 and added to the metal solutions. The mixture was vigorously stirred for 30 minutes, and the phases allowed

to separate. An aliquot (1 cm^3) of the aqueous layer was transferred to a sample tube, diluted to 5 cm^3 and analysed by ICP-OES. 1 cm^3 of the stock solution was diluted to 5cm^3 and counted. The amount of metal in the organic solution was the difference between this standard and experimentally measured sample. The results presented below are an average of three runs.

In order to determine distribution ratios of radioisotopes, the metal solution was placed in a sample vial and made up to 5 cm^3 with a buffer solution. The required amount of extractant was dissolved in 5 cm^3 of FC-72 and added to the metal solutions. The mixture was vigorously stirred for 30 minutes at 25°C, and the phases allowed to separate. An aliquot (1 cm^3) of each layer was transferred to a polypropylene tube and counted for γ activity. For strontium and uranium experiments an aliquot of each layer (1 cm^3) was transferred to a scintillation vial, diluted with scintillation cocktail (5 cm^3) and counted for β and α activities respectively.

L	L	D_{As} (%)	D_{Cr} (%)	D_{Co} (%)	D_{Cd} (%)	D_{Hg} (%)	D_{Sn} (%)	D_{Pb} (%)
$Rf_3P=O$	1	12.83 (92.8)	2.098 (76.9)	3.328 (100.0)	1.199 (100)	2.498 (89.4)	3.170 (100)	2.261 (85.0)
	2	a (100)	2.140 (77.4)	2.990 (94.9)	b (100)	2.472 (89.0)	c (100)	2.223 (84.4)
	3	a (100)	3.559 (78.1)	17.592 (94.6)	b (100)	2.456 (88.7)	c (100)	2.245 (84.8)
$Rf_3P=S$	1				20.182	0.873		
	2				20.182	1.039		
$Rf_2P(O)CH_2CH_2P(O)Rf_2$	1	0.916 (91.7)	1.080 (100)	0.812 (98.7)	1.108 (100)	1.063 (100)	0.533 (53.3)	1.053 (100)
	2	0.712 (72.6)	0.387 (38.8)	d (100)	1.082 (100)	1.093 (100)	0.397 (39.7)	0.966 (96.6)

a – with more than one equiv. of ligand, there was no As detected in the aqueous layer (limit of detection = 10 ppb)

b - with more than one equiv. of ligand, there was no Cd detected in the aqueous layer (limit of detection = 10 ppb)

c - with more than one equiv. of ligand, there was no Sn detected in the aqueous layer (limit of detection = 10 ppb)

d – with 2 equiv of ligand there was no Co detected in the aqueous layer (limit of detection = 5 ppb)

Table 1. Extraction of selected metals from water into FC-72 (Rf = $CF_3(CF_2)_5CH_2CH_2$).

Ligand	D_{Cd}
$\{CF_3(CF_2)_5CH_2CH_2\}_3P=O$	2.50
$\{CF_3(CF_2)_9CH_2CH_2\}_3P=O$	2.43

Table 2. Extraction of Cd^{2+} from water into FC-72 using different ligands

L	L	D_{Fe}	D_U	D_{Sr}	D_{Ba}
$Rf_3P=O$	1	0.100		a	1.922
	2	0.076		a	1.745
	3	0.003		a	-
$Rf_2P(O)CH_2CH_2P(O)RF_2$	1	0.119	1.709	0.015	b
	2	0.352	2.164	0.013	b
	3	2.310	1.646	0.036	b

a – ^{90}Sr in organic layer was below the limit of detection

b – ^{133}Ba in organic layer was below the limit of detection

Table 3. Extraction of selected radionuclides from water into FC-72.

Metal Complexes. The required amount of ligand and metal salt was mixed in CD_3OD in an NMR tube. This was sonicated for 15 minutes and the NMR spectra taken.

Pb: 0.034g $Pb(NO_3)$ and 0.30 g ligand. MPt (°C): 52-58; ^1H NMR 2.24 (m, 4H) 2.52 (m, 4H); ^{31}P NMR 51.43 ppm ($^2J_{Pb-P}$ = 69 Hz); ^{19}F -83.50 (m, CF_3), -117.29 (m, CF_2), -119.05 (m, CF_2), -124.80 (m, CF_2), -127.91 (m, CF_2), -128.23(m, CF_2); IR: 2957 (w), 1445 (w), 1366 (w), 1318 (w), 1171 (s), 1084 (s), 1022 (w), 936 (m), 819 (w) 777 (m), 709 (m), 650 (m), 566 (m), 528 (m), 448 (w); m/z [%]:1089 [L+H, 100%].

Cd: 0.013 g $CdCO_3$ and 0.12 g ligand. MPt (°C): 48-54; ^1H NMR: 2.36 (m, 4H) 2.43 (m, 4H); ^{31}P NMR: 47.48 ppm ($^2J_{Cd-P}$ = 33 Hz); ^{19}F NMR: -81.50 (t, $^3J_{F-F}$ = 10 Hz, CF_3), -115.07 (m, CF_2), -122.16 (m, CF_2), -123.38 (m, CF_2), -123.62 (m, CF_2), -126.70(m, CF_2); ^{13}C 19.21 (d, J_{C-P} = 68 Hz), 24.11 (t, J_{P-C} = 22 Hz), 109.1 (m), 111.8 (m), 114.1 (m), 116.4 (m), 119.1 (m), 122.3 (m); IR (cm^{-1}): 2957 (w), 1445 (w), 1366 (w), 1318 (w), 1171 (s), 1084 (s), 1022 (w), 936 (m), 819 (w) 777 (m), 709 (m), 650 (m), 566 (m), 528 (m), 448 (w); m/z [%]:1203 [LCd, 5%], 1089 [L+H, 50%].

Perfluoro(butyltetrahydrofuran) solvent (FC75)

Cd was extracted from water using FC-75 as a solvent with $\{CF_3(CF_2)_5CH_2CH_2\}_3P{=}O$. The experiment showed that the percentage extraction for 1 equivalent was 35.6% and for two equivalents 38.7%

Solution Extraction Studies.

A stock solution of uranyl nitrate was diluted to 5 cm^3 using distilled water to give 0.02g uranyl nitrate. The required amount of the ligand was dissolved in freshly distilled perfluoromethylcyclohexane (5 cm^3) and the two solvents mixed. The biphasic mixture was vigorously stirred for 30 minutes then the two layers separated. 1 cm^3 of each sample was transferred to a cuvette and the uv-vis spectrum recorded.

NMR Studies.

The required amount of ligand and metal salt was mixed in CD_3OD in an NMR tube. This was sonicated for 15 minutes and the NMR spectra taken.

Pb: 0.034g $Pb(NO_3)$ and 0.30 g ligand. MPt (°C): 52-58; ^1H NMR 2.24 (m, 4H) 2.52 (m, 4H); ^{31}P NMR 51.43 ppm ($^2J_{Pb\text{-}P}$ = 69 Hz); ^{19}F -83.50 (m, CF_3), -117.29 (m, CF_2), -119.05 (m, CF_2), -124.80 (m, CF_2), -127.91 (m, CF_2), -128.23(m, CF_2); IR: 2957 (w), 1445 (w), 1366 (w), 1318 (w), 1171 (s), 1084 (s), 1022 (w), 936 (m), 819 (w) 777 (m), 709 (m), 650 (m), 566 (m), 528 (m), 448 (w); m/z [%]:1089 [L+H, 100%].

Cd: 0.013 g $CdCO_3$ and 0.12 g ligand. MPt (°C): 48-54; ^1H NMR: 2.36 (m, 4H) 2.43 (m, 4H); ^{31}P NMR: 47.48 ppm ($^2J_{Cd\text{-}P}$ = 33 Hz); ^{19}F NMR: -81.50 (t, $^3J_{F\text{-}F}$ = 10 Hz, CF_3), -115.07 (m, CF_2), -122.16 (m, CF_2), -123.38 (m, CF_2), -123.62 (m, CF_2), -126.70(m, CF_2); ^{13}C 19.21 (d, $J_{C\text{-}P}$ = 68 Hz), 24.11 (t, $J_{P\text{-}C}$ = 22 Hz), 109.1 (m), 111.8 (m), 114.1 (m), 116.4 (m), 119.1 (m), 122.3 (m); IR (cm^{-1}): 2957 (w), 1445 (w), 1366 (w), 1318 (w), 1171 (s), 1084 (s), 1022 (w), 936 (m), 819 (w) 777 (m), 709 (m), 650 (m), 566 (m), 528 (m), 448 (w); m/z [%]:1203 [LCd, 5%], 1089 [L+H, 50%] .

RESULTS

$\{CF_3(CF_2)_5CH_2CH_2\}_3P{=}O$ with uranyl acetate and nitrate

The reactions of the ligand $\{CF_3(CF_2)_5CH_2CH_2\}_3P{=}O$ with uranyl acetate and nitrate has been examined via UV-vis and infrared spectroscopy. Thus the ligand-uranyl acetate reaction shows a significant change in the UV-Vis spectrum [Figure 3(a)] upon the addition of three equivalents of the ligand whilst the U=O and P=O stretch in the infrared spectrum also shifts relative to the free compounds [Figure 3(b)]. In order to ascertain the optimum ligand:uranyl ratio, the absorbance of the peak at 352nm was measured against ligand concentration (Figure 4). In this experiment a known amount of uranyl nitrate was dissolved in water and a solution of the ligand in perfluoromethylcyclohexane added. After stirring for ½ hr at 30°C the phases were separated and the fluorous phase examined spectroscopically. The use of a fluorous solvent as a model for *sc*CO_2 is well known. The data suggests that a 3:1 complex is formed, but upon addition of further equivalents of ligand an as yet unknown compound is formed which is possibly a dimeric species of the formulation $[\{(UO_2)(Rf_3P{=}O)_3\}_2(\mu\text{-}Rf_3P{=}O)_2][NO_3]_4$.

The reaction of the ligand with Tin(IV), Cadmium (II) and Lead(II) was also investigated via ^{31}P NMR spectroscopy and the observation of tin and lead satellites clearly demonstrate coordination of the ligand to these metal ions (Figure 5). The resulting complexes have good solubility in fluorinated solvents, indicating their solubility in *sc*CO_2.

From these observations, the ligand $\{CF_3(CF_2)_5CH_2CH_2\}_3P{=}O$ can extract a variety of metals into a fluorous solvent.

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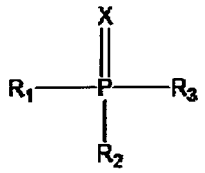
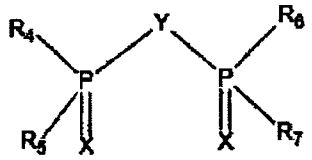
Claims

1. A method for extracting a metal comprising: exposing a metal containing material to (i) liquid solvent or supercritical solvent; in combination with (ii) a perfluorinated phosphine.

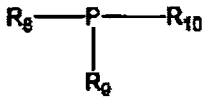
2. A method according to claim 1 wherein the perfluorinated phosphine has a general formula I, II or III where:



I



II



III

each of groups R1, R2, R3, R4, R5, R6, R7, R8, R9 and R10, are independently selectable and are branched, straight or cyclic fluorocarbon groups, optionally comprising one or more alkyl moieties, preferably having the general formula $CF_3(CF_2)_n(CH_2)_m$, wherein one or more adjacent groups may be joined to form one or more rings where;

m is an integer of 1, 2, 3, 4, 5, 6, 7, 8, 9 or 10
n is an integer from 0-20
X is O or S
Y is a linker group

3. A method according to claim 2, wherein m = 2 or 3.

4. A method according to claim 2 or claim 3 wherein n is an integer selected from 3, 5, 7, 9 and 11.

5. A method according to claims 2 to 4, wherein x is O.

6. A method according to claims 2 to 5, wherein Y is a C1 to C6 alkyl group.

7. A method according to any preceding claim additionally comprising exposing the metal containing material to an oxidising agent.

8. A method according to any preceding claim where the solvent is an organohalide.

9 A method according to claim 8, wherein the solvent is perfluorinated.

10 A method according to claims 1 to 7, wherein the supercritical solvent is carbon dioxide.

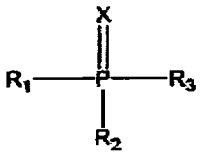
11. A method according to any preceding claim wherein the metal-containing material is selected from soil, laboratory clothing or other laboratory waste, and laboratory utensils.

12. A method according to any preceding claim wherein the metal is selected from one or more of cadmium, strontium, plutonium, uranium, lead, mercury chromium, arsenic, antimony, tellurium, polonium, germanium and salts thereof.

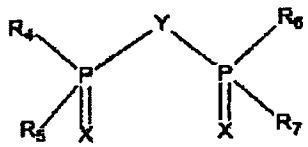
13. A method according to any preceding claim additionally comprising the steps of separating the solvent form the perfluorinated phosphine.

14. In combination, (i) a solvent and (ii) a perfluorinated phosphine, coordinated to a metal selected from one or more of cadmium, strontium, plutonium, uranium, lead, mercury chromium, arsenic, antimony, tellurium, polonium, germanium and salts thereof.

15. The combination according to claim 14, wherein the perfluorinated phosphine has a general formula I, II or III where:



I



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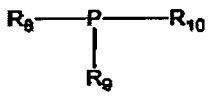


III

each of groups R1, R2, R3, R4, R5, R6, R7, R8, R9 and R10, are independently selectable and are branched, straight or cyclic fluorocarbon groups, optionally comprising one or more alkyl moieties, preferably having the general formula $CF_3(CF_2)_n(CH_2)_m$, wherein one or more adjacent groups may be joined to form one or more rings where;

m is an integer of 1 to 10, and n is an integer of 0 to 20.

x = O or S

y = a linker group

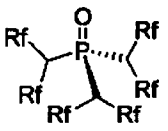
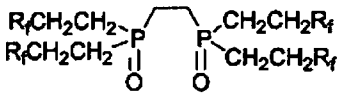
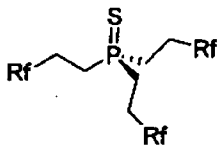
16. The combination according to claim 15, wherein m = 2 or 3.

18. The combination according to claim 15 or claim 16, wherein x is O.

19. The combination according to claims 15 to 17, where Y is a C1 to C6 alkyl.

20. The combination according to claims 15 to 19, wherein the solvent is carbon dioxide or a perfluorinated organohalide .

21. A perfluorinated phosphine selected from:

$(Rf(CH_2)_y)_3P$   

Where $Rf = CF_3(CF_2)_n$

n = an integer of 1-20

y = 3 or 4

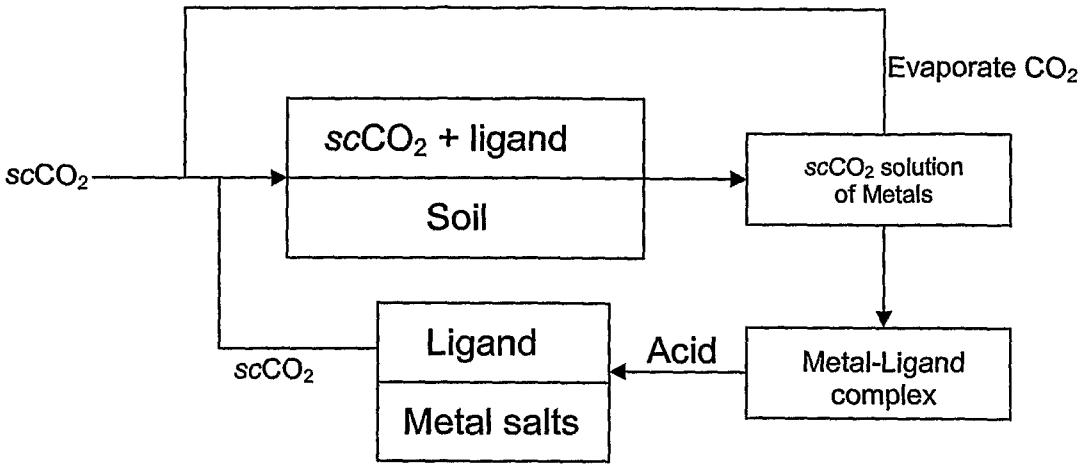

Evaporate CO_2
$scCO_2$ + ligand
Soil
$scCO_2$
$scCO_2$ solution of Metals
Ligand
Metal salts
$scCO_2$
Acid
Metal-Ligand complex

Figure 1

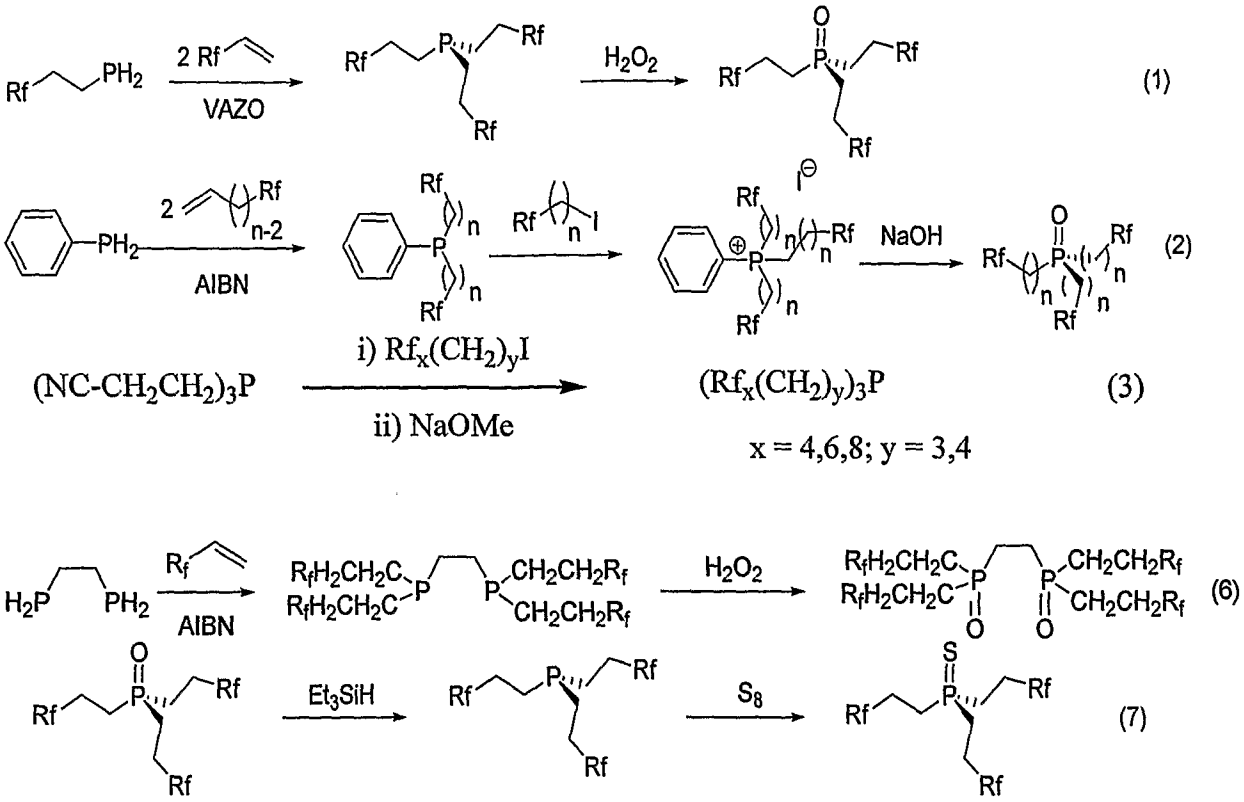

2 Rf
VAZO
H_2O_2
(1)
2
n-2
AIBN
NaOH
(2)
$(NC\text{-}CH_2CH_2)_3P$
i) $Rf_x(CH_2)_yI$
ii) NaOMe
$(Rf_x(CH_2)_y)_3P$
(3)
x = 4,6,8; y = 3,4
R_f
AIBN
H_2O_2
(6)
Et_3SiH
S_8
(7)

Figure 2

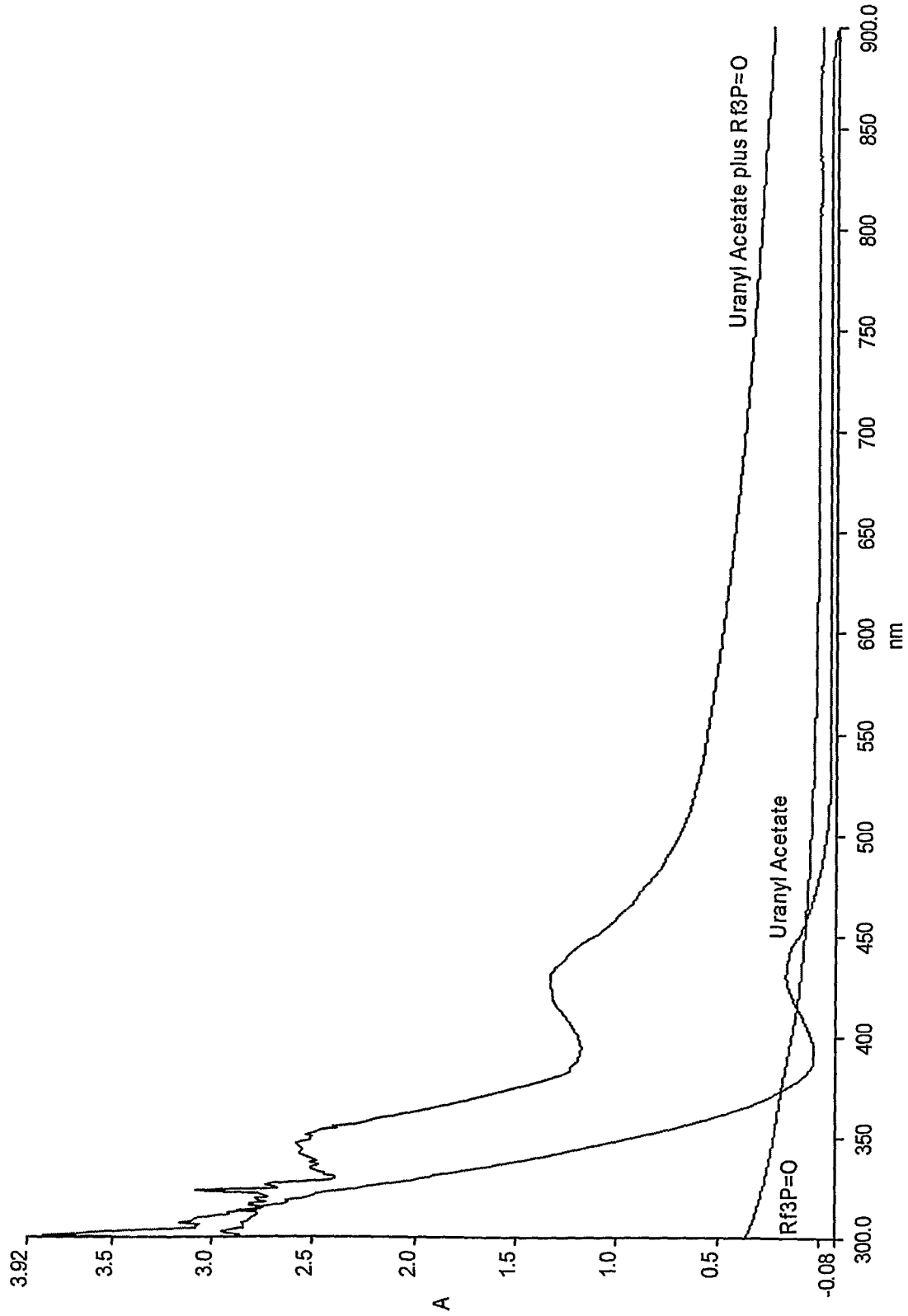

Uranyl Acetate plus Rf3P=O
Uranyl Acetate
Rf3P=O
A
nm
3.92
3.5
3.0
2.5
2.0
1.5
1.0
0.5
-0.08
300.0
350
400
450
500
550
600
650
700
750
800
850
900.0

Figure 3a

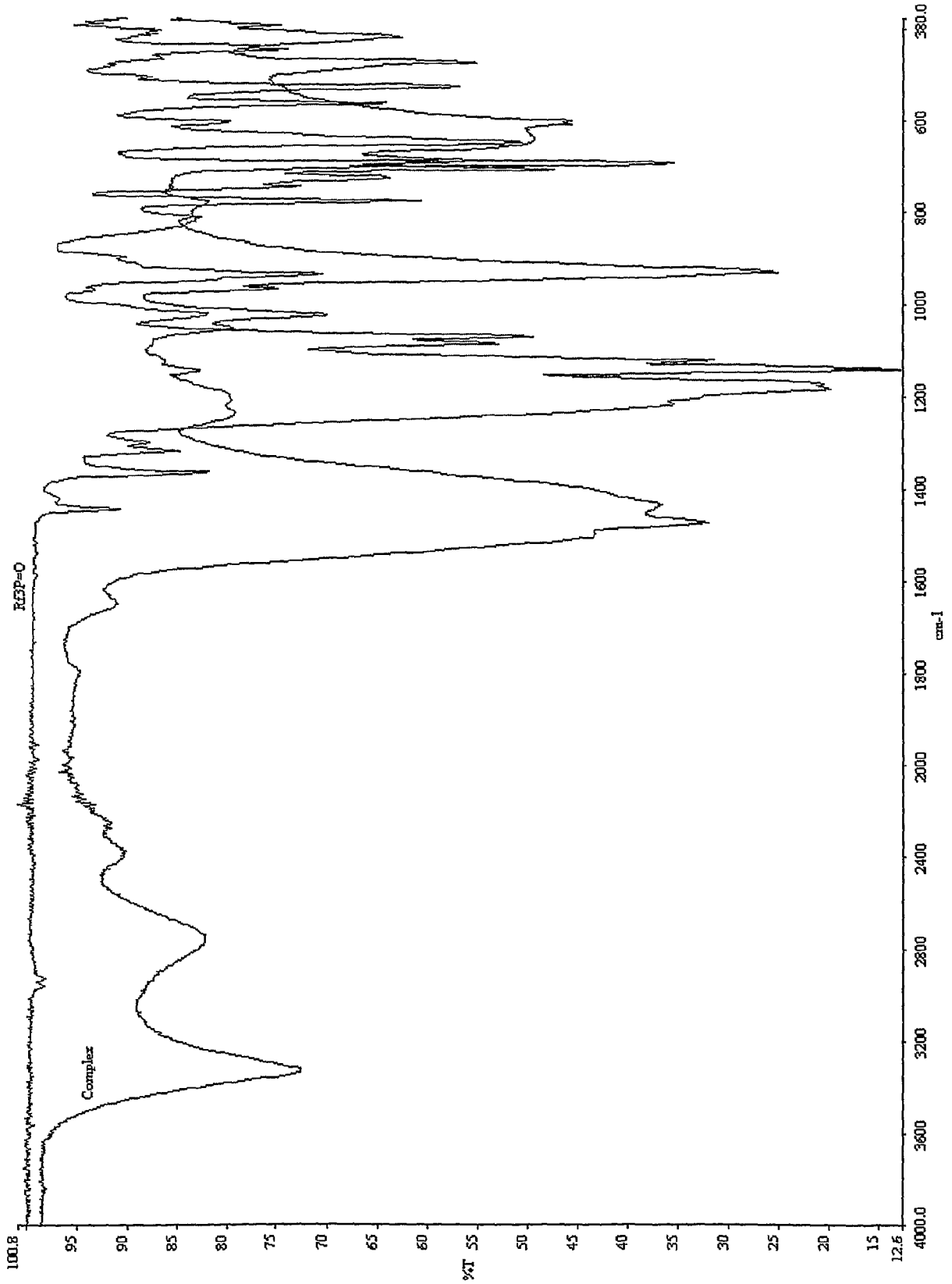

R3P=O
Complex
%T
cm-1
4000.0
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
600
400.0
100.8
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
12.6

Figure 3b

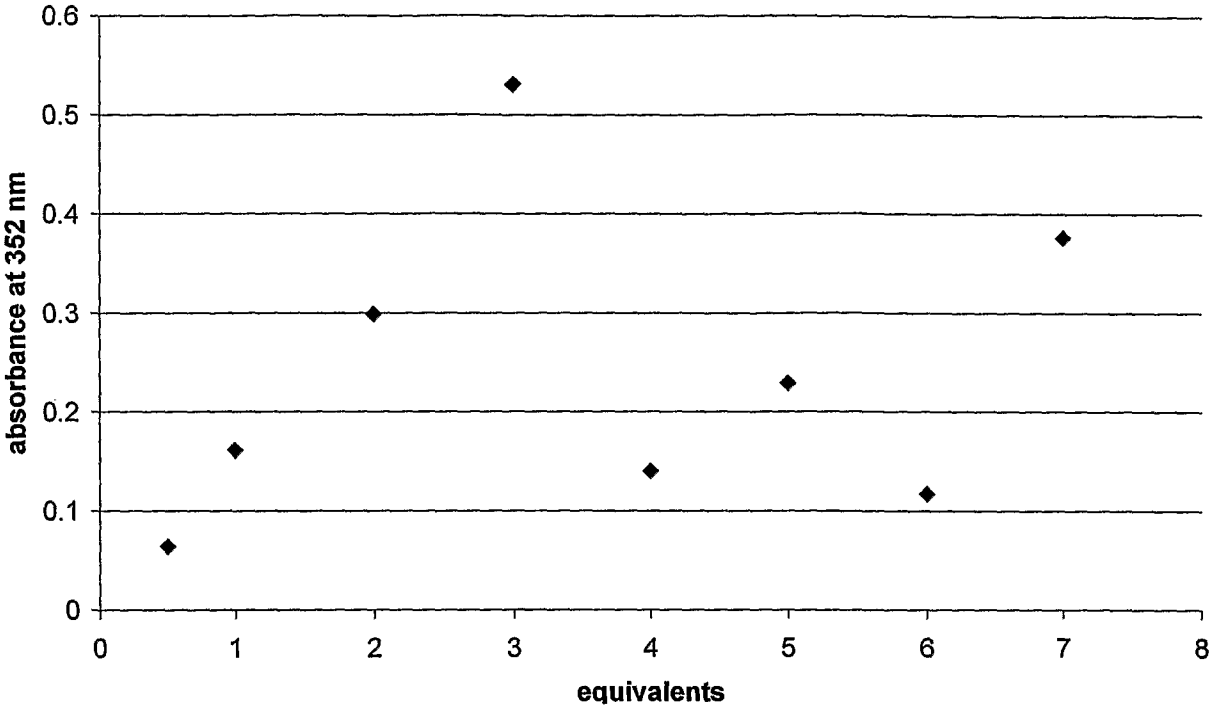

0.6
0.5
0.4
0.3
0.2
0.1
0
absorbance at 352 nm
0
1
2
3
4
5
6
7
8
equivalents

Figure 4

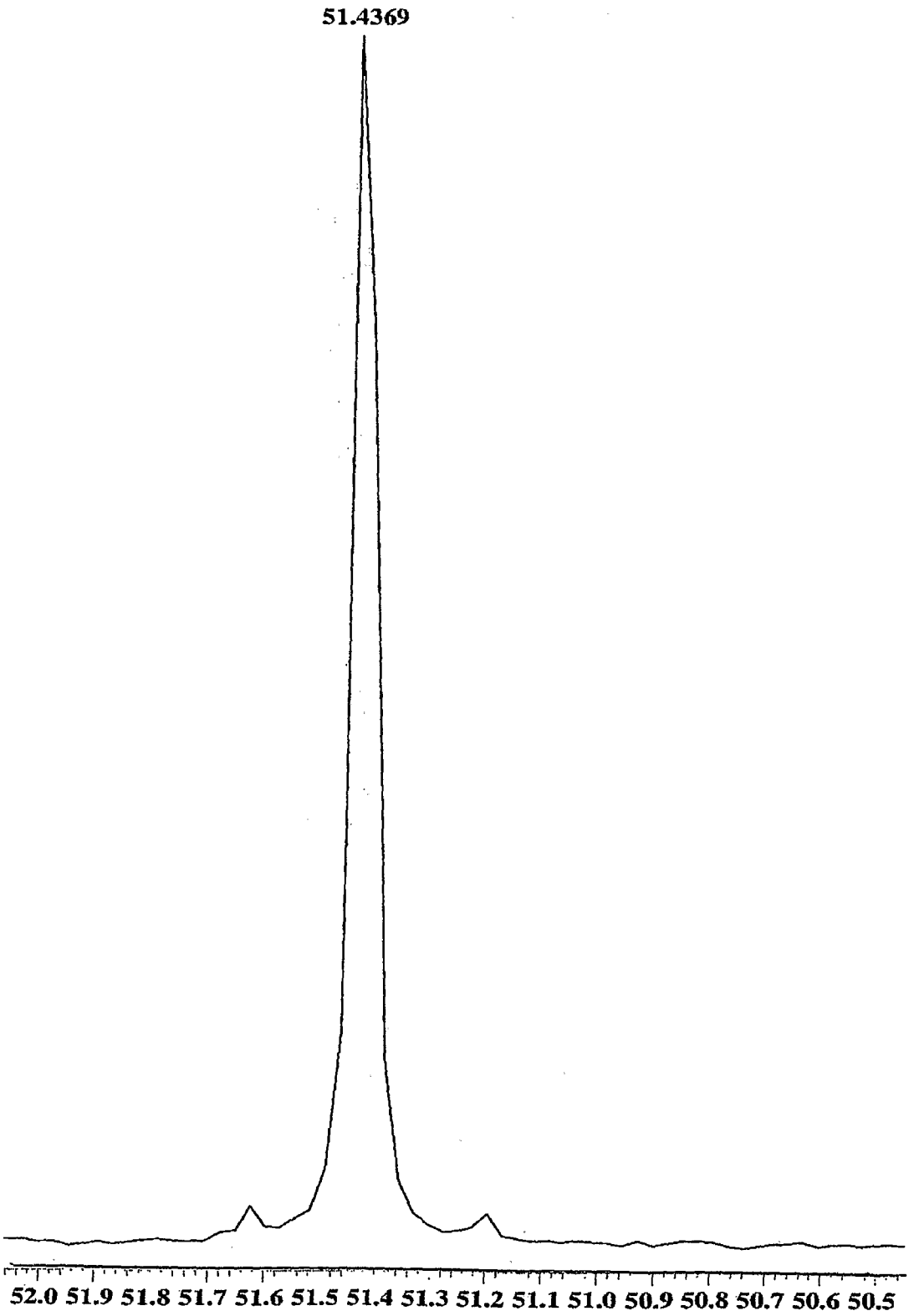

51.4369
52.0 51.9 51.8 51.7 51.6 51.5 51.4 51.3 51.2 51.1 51.0 50.9 50.8 50.7 50.6 50.5

Figure 5a

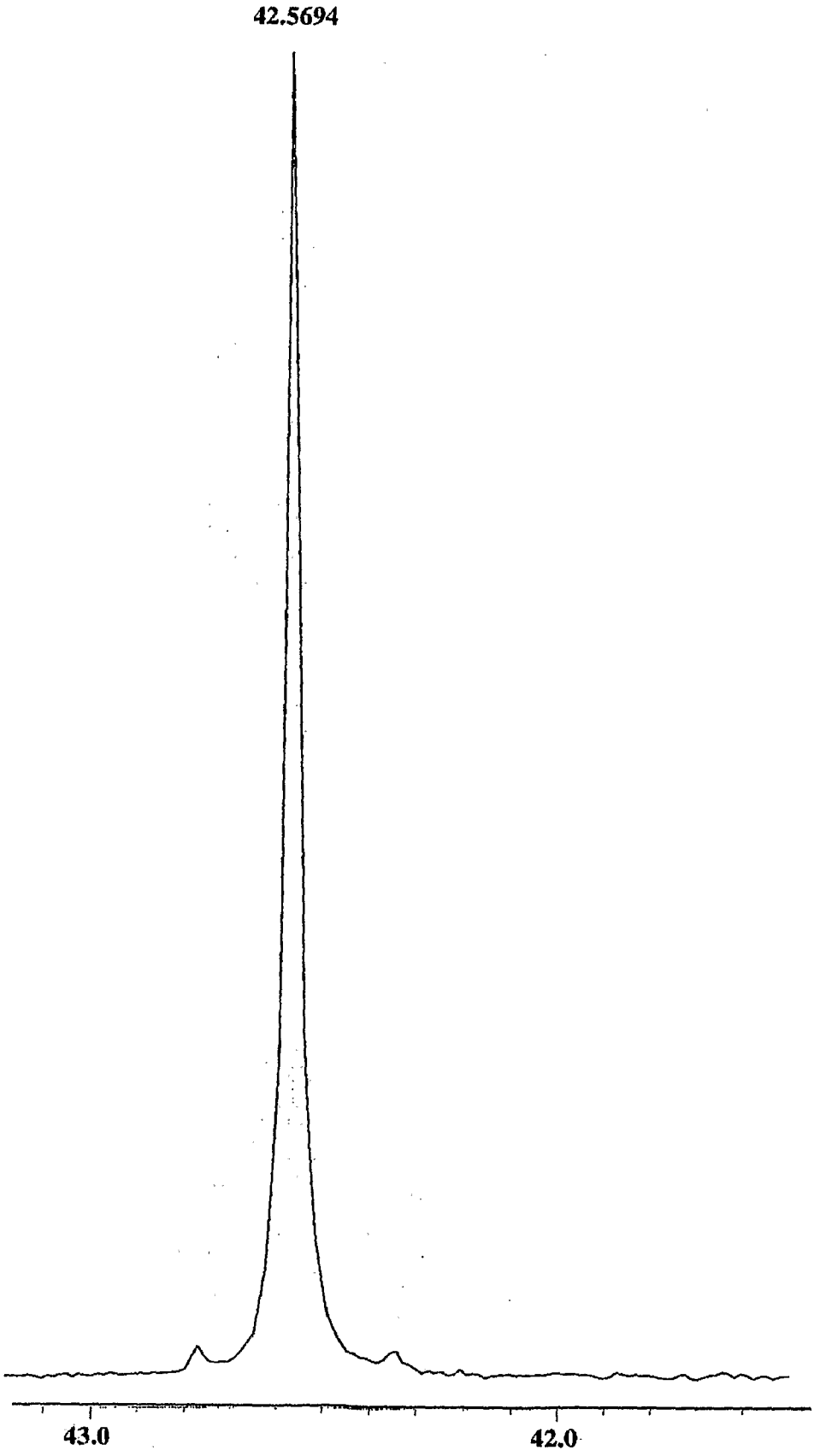


Figure 5b

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2009/000602

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01D11/02 C22B3/00 B08B7/00 B09C1/02 G21F9/28
C11D11/00 D06F43/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B01D C22B B08B B09C G21F C11D D06F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2006/113621 A (ADVANCED TECH MATERIALS [US]; VISINTIN PAMELA M [US]; KORZENSKI MICHAE) 26 October 2006 (2006-10-26) claims 1,5,18,22	1-10, 12-21
X	WO 99/38820 A (UNIV CAMBRIDGE TECH [GB]; HOLMES ANDREW BRUCE [GB]; COOPER ANDREW IAN) 5 August 1999 (1999-08-05) page 3, line 31 - page 4, line 25; claims 1,6	14-21
A	WO 98/04754 A (IDAHO RES FOUND [US]) 5 February 1998 (1998-02-05) claims 1,6,8	

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
8 May 2009	20/05/2009
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	**Authorized officer** Roider, Josef

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/GB2009/000602

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2006113621 A	26-10-2006	CN 101198416 A	11-06-2008
		EP 1879704 A2	23-01-2008
		JP 2008537343 T	11-09-2008
		KR 20070120609 A	24-12-2007
		US 2008269096 A1	30-10-2008
WO 9938820 A	05-08-1999	AU 2290399 A	16-08-1999
		DE 69912097 D1	20-11-2003
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		CN 1226286 A	18-08-1999
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		EP 0914482 A1	12-05-1999
		ES 2173472 T3	16-10-2002
		JP 2000515932 T	28-11-2000
		KR 20000029570 A	25-05-2000
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