TECHNICAL DESCRIPTION

In order to solve the problems described above, an **extractant mixture consisting of a TSIL process ionic liquid** (see chemical formula in *Figure 1*) **dissolved in an IL ionic liquid** (see chemical formula in *Figure 2*) has been developed.



Figure 1: TSIL compound.



Figure 2: Ionic liquid IL (CYPHOS NTf₂).

This extractant mixture is characterised by the fact that it allows the **selective liquid-liquid extraction** of **f-block metals** of the periodic table (lanthanide and actinide series) in samples containing other metals of the s-, p- and/or d-series.

The procedure to prepare the above **TSIL compound** is carried out in a very simple way from the antibiotic ciprofloxacin using conventional functional group transformations. The synthesis of this compound takes place in **three steps** under mild reaction conditions (room temperature to 0° C, atmospheric air pressure, etc.).

Step 1: N-alkylation reaction of ciprofloxacin with 1-bromoethane in the presence of excess N,N-diisopropyl(ethyl)amine to generate the following intermediate (see *Figure 3*) in 88% yield:



Figure 3: Reaction intermediate.

Step 2: Amidation reaction of the above compound using an excess of N,Odimethylhydroxylamine in the presence of thionyl chloride to give the following Weinreb's amide (see *Figure 4*) in 86% yield:



Figure 4: Weinreb's amide.

Stage 3: Alkylation reaction of the above compound by the addition of excess 1iodonononane and subsequent ion exchange with lithium bis(trifuromethanesulfonyl)amidide to obtain the above **TSIL molecule** (see *Figure 1*) in **92% yield**.

On the other hand, the **procedure for the selective extraction of f-block metals** in a sample containing **f-block metals** together with other s-, p- and/or d-series metals are as follows:

- 1) Prepare the extractant mixture (B) consisting of the compound TSIL from Figure 1 and the ionic liquid CYPHOS NTf₂ from *Figure 2*.
- Place the sample to be separated (A) containing one or more f-block metal(s) and other metals belonging to the s-, p- and/or d-series into a test tube. Adjust the pH to 6.
- 3) Add the extractant mixture (B) to the sample to be separated (A).
- 4) Shake for at least three minutes.
- 5) Wait until two liquid-liquid phases of different densities are differentiated.
- 6) Separate the two phases, the organic phase being the one corresponding to the extractant mixture (B) which includes the metal (or metals) of block f initially contained in the sample to be separated (A) (see *Figure 5*).



Figure 5: Schematic of the selective extraction process.

- 7) Add to the recovered organic phase (B) an acidified solution at pH=0.5 (C).
- 8) Stir.
- 9) Wait until two liquid-liquid phases of different densities are differentiated.
- 10)Separate the two phases, where the organic phase corresponds to the metal-free extractant mixture (B) and the aqueous phase (C) containing the metal(s) of f-block (see *Figure 6*).



Figure 6: Schematic of the recovery process of the extractant mixture.

CURRENT STATE OF THE TECHNOLOGY

The technology described has been developed on a **laboratory scale** (state of Technological Readiness Level: **TRL = 3**).

Tests have shown very promising results. A table with the **analyte distribution coefficient** (\mathbf{K}), which is the ratio of the concentration of the metal in the organic phase to its concentration in the aqueous phase after the extraction procedure, is shown below (see *Table 1*).

f-series metals	K	s-, p- and d-	K
		series metals	
Th	746.4	Li	1.7
U	845.5	Al	1.1
Lu	479.3	Ti	13.7
Yb	441.6	V	1.8
Gd	433.9	Cr	2.3
Nd	394.2	Mn	1.6
Sm	600.5	Fe	11.3
La	178.8	Со	1.0
Y	146.2	Ni	1.0
Се	327.5	Cu	9.9
Eu	614.3	Zn	24.2
Sc	1683.1	Ga	3.8
Pr	306.9	As	1.1
Tb	527.4	Se	1.0
Dy	188.9	Zr	3.2
Ho	106.8	Мо	1.3
Er	206.7	Ru	1.5
Tm	357.2	Pd	2.2
		Ag	42.1
		Cd	1.3
		In	4.1
		Sn	4.7
		Sb	1.1
		Te	2.4
		Pt	1.0
		Au	1.0
		Hg	43.7
		TI	1.0
		Pb	3.4
		Bi	2.7
		Rh	1.1
		Re	1.1

Table 1: The value of the distribution coefficients (K) obtained for the f-series metals, as well as for other metallic elements of the periodic table that can be found in their presence, at pH=6.

These tests have demonstrated the **high efficiency and selectivity** of the extractant mixture, since the higher the distribution coefficient of the analyte (K), the higher the extraction efficiency.

TECHNICAL KEYWORDS

TSIL, Task Specific Ionic Liquids, Ionic Liquid, extraction, selective, extraction, lanthanides, actinides, rare earths, recycling, mining, nuclear, chemical, medical, waste, ciprofloxacin, waste, ciprofloxacin.