Is it easy to improve radiochemical methods in respect of REACH regulation?

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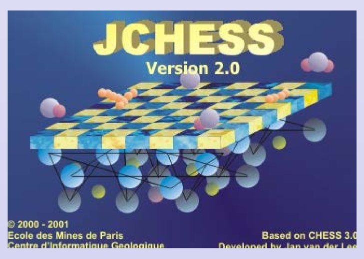
For more than twenty years, the LASE (Operator Support Analysis Laboratory) has been developing and implementing radiochemical methods devoted to the determination of Difficult To Measure radionuclides in radwaste. In particular, its expertise concerns the characterization of long-lived beta emitters such as **^{63}Ni, ^{55}Fe and ^{99}Tc** in various matrices. The purification procedures applied for a long time are highly selective towards those radionuclides but mainly based on liquid-liquid extraction steps including the use of chloroform [1-3] which is restricted through REACH regulation. The elimination of this solvent is a real challenge for radioanalytical laboratories. Furthermore, the supply of radioactive tracers such as ^{99m}Tc is becoming difficult. Consequently, alternative radiochemical methods were investigated: extraction chromatography [2,4,5] was compared to liquid-liquid extraction towards ^{63}Ni, ^{55}Fe and ^{99}Tc analysis.

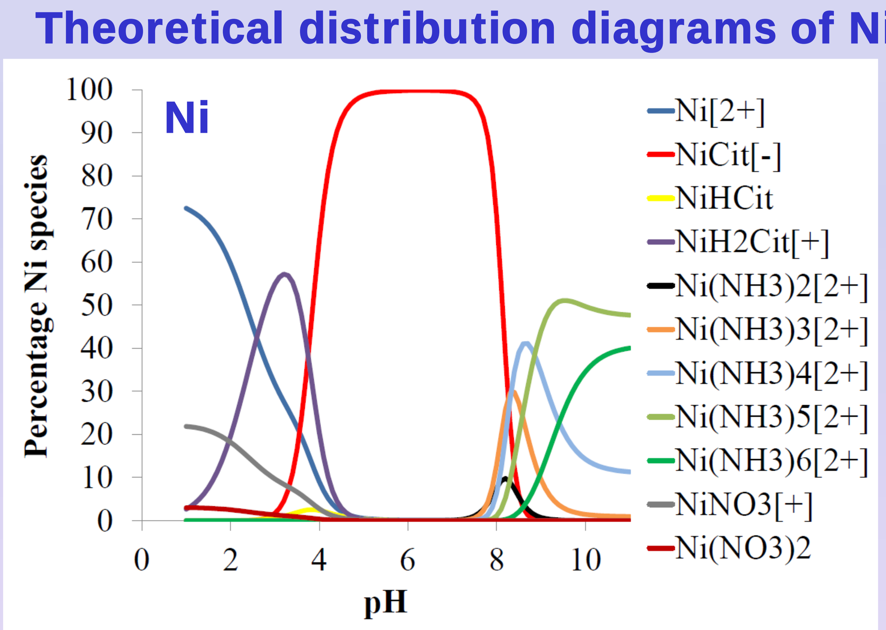
Preliminary speciation calculations to optimize the alternative radiochemical methods

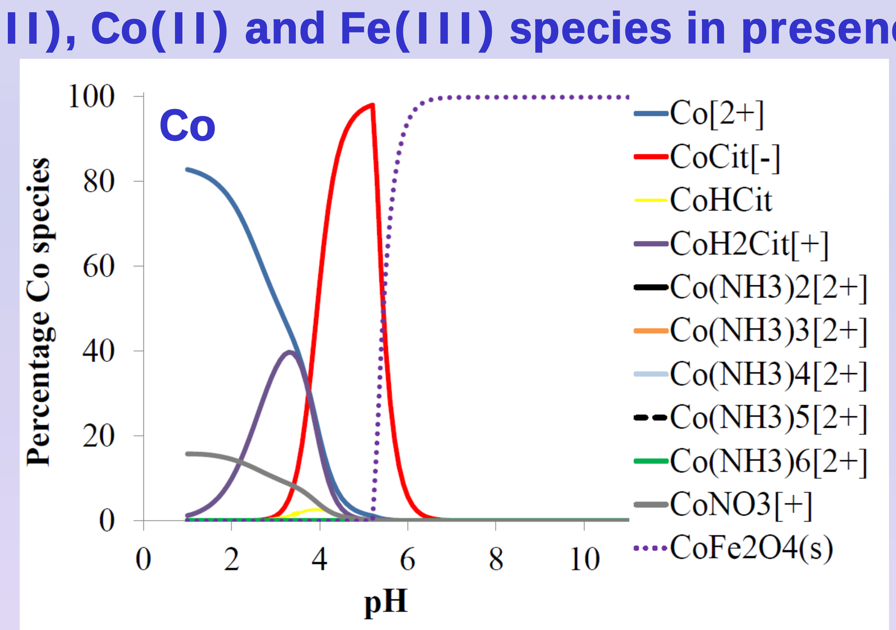


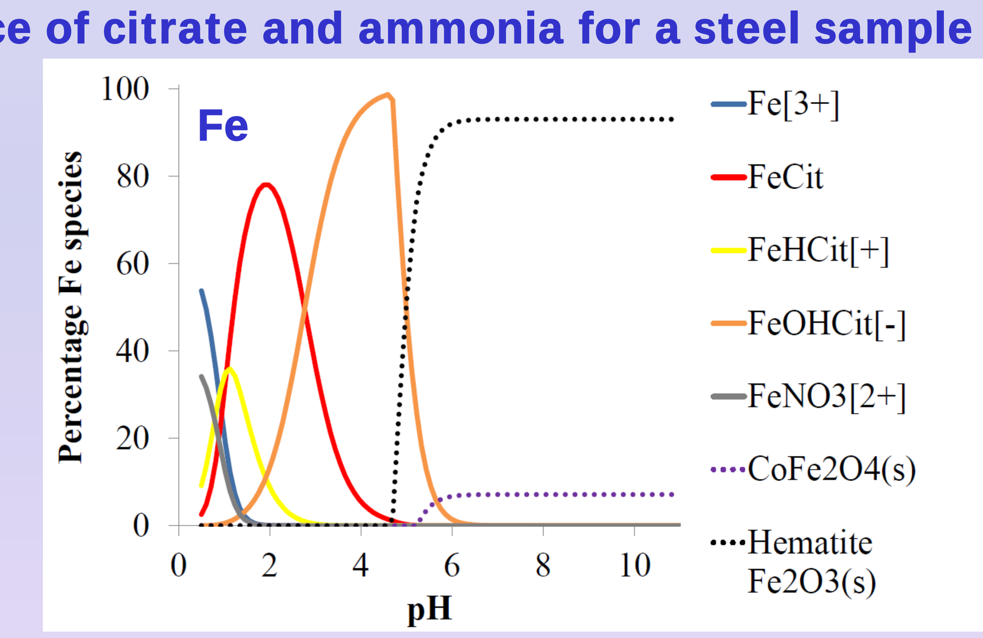
Implementation of JChess® software: enrichment of its database with specific stability constants of Ni, Co and Fe with ammonia, citrate, tartrate and other ligands of interest (ex: dimethylglyoxime DMG)

Composition of a digested steel	
Fe	800 mg/L
Co	30 mg/L
Ni	5 mg/L
NH_3	0 → 1 mol/L
citrate	0.25 mol/L

Theoretical distribution diagrams of Ni(II), Co(II) and Fe(III) species in presence of citrate and ammonia for a steel sample





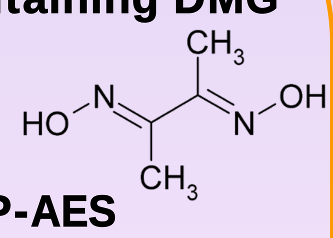


→ **Better understanding of analytes behavior during radiochemical procedures with speciation calculations**

^{63}Ni determination in radwaste

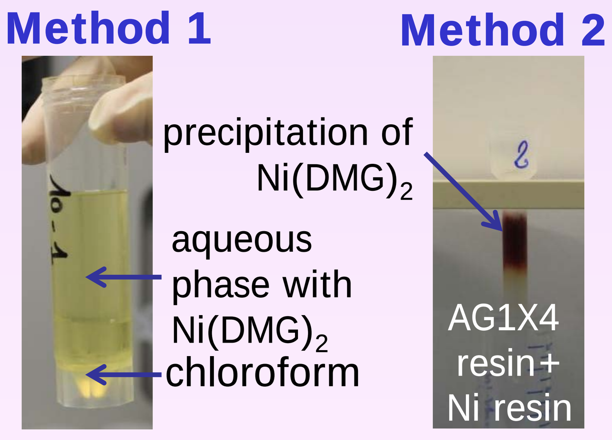
Purification method: liquid-liquid extraction (Method 1) versus extraction chromatography (Method 2) based on Ni® resin containing DMG

Detection technique: LSC



Recovery yield: measurement of stable Ni tracer by ICP-AES

- Sample digestion
- Addition of Ni and citric acid
- Method 1 or Method 2
- LSC and ICP-AES



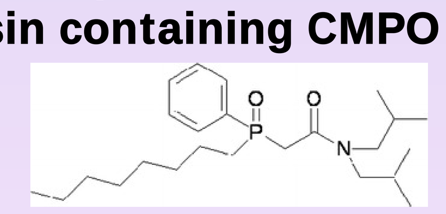
Sample	Recovery yield (%) Method 1	Recovery yield (%) Method 2	^{63}Ni (Bq/g) Method 1	^{63}Ni (Bq/g) Method 2
Sludge	86	101	2.76x10^2 ± 5 %	2.88x10^2 ± 5 %
Steel	69	98	3.99x10^3 ± 5 %	3.82x10^3 ± 5 %
Polymer	82	100	3.48x10^5 ± 4 %	3.50x10^5 ± 4 %

→ **Effective extraction chromatography method based on Ni® resin when associated to anion-exchange resin [2]**

^{55}Fe determination in radwaste

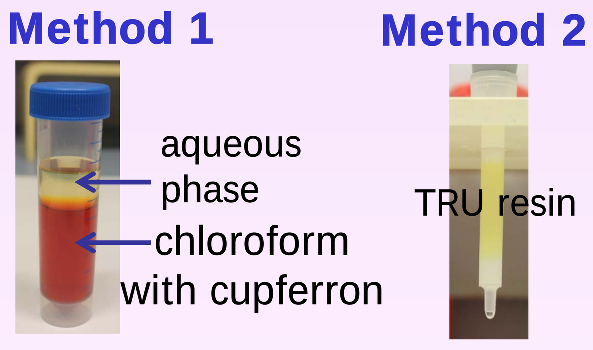
Purification method: liquid-liquid extraction (Method 1) versus extraction chromatography (Method 2) based on TRU® resin containing CMPO

Detection technique: LSC



Recovery yield: measurement of stable Fe tracer by ICP-AES

- Sample digestion
- Precipitation with NH_3
- Separation on anion-exchange AG1X4 resin
- Method 1 [3] or Method 2
- LSC and ICP-AES



Sample	Recovery yield (%) Method 1	Recovery yield (%) Method 2	^{55}Fe (Bq/g) Method 1	^{55}Fe (Bq/g) Method 2
Aluminium	72	82	3.70x10^5 ± 8 %	3.62x10^5 ± 8 %
Steel	23	80	3.80x10^3 ± 7 %	3.73x10^3 ± 7 %
Ion-exchange resin	74	86	2.62x10^3 ± 5 %	2.50x10^3 ± 5 %

→ **Effective extraction chromatography method based on TRU® resin when associated to anion-exchange resin**

^{99}Tc determination in radwaste

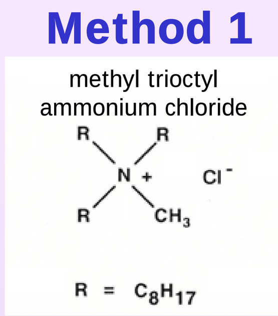
Purification method: home-made extraction chromatography (Method 1) versus extraction chromatography (Method 2) based on TEVA® resin

Detection technique: LSC and ICP-MS Q

Recovery yield: measurement of ^{99m}Tc tracer by γ-spectrometry and Re tracer by ICP-AES

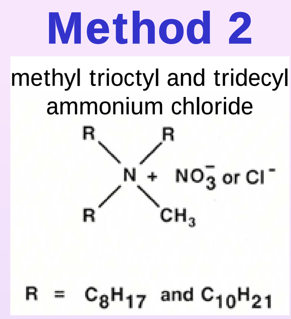
- Alkali fusion with ^{99m}Tc and Re
- Method 1 [1] or Method 2 [5]
- Liquid-liquid extraction with BPHA [1]
- LSC, γ-spectrometry versus ICP-AES

Method 1



home-made resin with CMTO [1]

Method 2



TEVA® resin [4-5]

Sample	Recovery yield based on ^{99m}Tc (%) Method 1	Recovery yield based on Re (%) Method 1	Recovery yield based on ^{99m}Tc (%) Method 2	^{99}Tc (Bq/g) Method 1 with ^{99m}Tc tracer	^{99}Tc (Bq/g) Method 2 with ^{99m}Tc tracer
Concrete	74	8	80	1.97 ± 12 %	1.93 ± 12 %
NPL solution - 2015 proficiency test exercise	84	6	88	0.54 ± 15 %	0.58 ± 15 %

→ **Effective replacement of home-made resin by TEVA® resin**
→ **Inappropriate replacement of ^{99m}Tc by rhenium when associated to liquid-liquid extraction based on BPHA**

Novel aspect

Speciation studies were of prime interest to foresee the analytes behavior during the development of alternative radiochemical separations. When associated to anion-exchange chromatography, extraction chromatography based on Ni®, TRU® and TEVA® resins was proved to be effective respectively for the determination of ^{63}Ni, ^{55}Fe and ^{99}Tc in various radwaste.

[1] Hepiegne et al., The separation of ^{99}Tc from low and medium-level radioactive wastes and its determination by inductively coupled plasma mass spectrometry, Talanta 41 (1995) 803-809.
[2] Gautier et al., A comparative study using liquid scintillation counting to determine ^{63}Ni in low and intermediate level radioactive waste, J. Radioanal. Nucl. Chem. 308 (2016) 261-270.
[3] AFNOR Standard NF M60-322 (2005) Nuclear energy - Nuclear fuel cycle technology - Waste - Determination of iron 55 activity in effluents and waste by liquid scintillation after prior chemical separation.
[4] Horwitz et al., Separation and Preconcentration of Actinides by Extraction Chromatography Using a Supported Liquid Anion Exchanger: Application to the Characterization of High-Level Nuclear Waste Solutions, Anal. Chim. Acta 310 (1995) 63-78.
[5] Shi et al., Determination of technetium-99 in environmental samples: A review, Anal. Chim. Acta 709 (2012) 1-20.