

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

C. Gautier, C. Colin, J. P. Degros, P. Perret, C. Cruchet, M. Giuliani, E.

Laporte, C. Mougel

► To cite this version:

C. Gautier, C. Colin, J. P. Degros, P. Perret, C. Cruchet, et al.. Is it easy to improve radiochemical methods in respect of REACH regulation?. NRC9 - 9th international conference on nuclear and radiochemistry, Aug 2016, Helsinki, Finland. hal-02442258

HAL Id: hal-02442258 https://cea.hal.science/hal-02442258

Submitted on 16 Jan 2020 $\,$

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers. L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

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



C. Gautier*, C. Colin, J.P. Degros, P. Perret, C. Cruchet, M. Giuliani, E. Laporte and C. Mougel

Den - Service d'Etudes Analytiques et de Réactivité des Surfaces (SEARS), CEA, Université Paris-Saclay, F-91191, Gif-sur-Yvette, France

*celine.gautier@cea.fr

9th INTERNATIONAL CONFERENCE ON NUCLEAR AND RADIOCHEMISTRY - NRC9

Helsinki (Finland) August 29 -September 2, 2016

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 ⁶³Ni, ⁵⁵Fe and ⁹⁹Tc 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 ⁶³Ni, ⁵⁵Fe and ⁹⁹Tc 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)

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

⁶³Ni 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

Recovery

Sample vield (%) vield (%)

Sample digestion

Addition of Ni and citric acid

Alkali fusion with ^{99m}Tc and Re

⁵⁵Fe determination in radwaste

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

Detection technique: LSC

⁵⁵Fe

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

Sample digestion

Precipitation with NH₂

Recovery Recovery ⁵⁵Fe

		Method 1	Method 2	Method 1	Method 2
Method 1 or Method 2 LSC and ICP-AES Method 1 Method 2	Sludge	86	101	2.76x10 ² ± 5 %	2.88x10 ² ± 5 %
precipitation of Ni(DMG) ₂	Steel	69	98	3.99x10 ³ ± 5 %	3.82x10 ³ ± 5 %
phase with Ni(DMG) ₂ -chloroform Ni resin +	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]

	Sample		yiela (70)	(Bq/g)	(b q/g)
Separation on anion-		Method 1	Method 2	Method 1	Method 2
exchange AG1X4 resin				2 70.105	2 (2, 105
Method 1 [3] or Method 2	Aluminium	72	82	3.70×10^{3} + 8 %	3.62×10^{3} + 8 %
LSC and ICP-AES				± 0 /0	± 0 70
Method 1 Method 2	Steel	23	80	3.80x10 ³ ± 7 %	3.73x10 ³ ± 7 %
phase TRU resin Chloroform with cupferron	lon- 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

⁹⁹Tc 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

Method 1 methyl trioctyl

Method 2

methyl trioctyl and tridecyl ammonium chloride

⁶³Ni

(Ba/a)

Recovery

⁶³Ni

(Ba/a)

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	99Tc (Bq/g) Method 2 with ^{99m} Tc tracer
Concrete	74	8	80	1.97 ± 12 %	1.93 ± 12 %
NPL solution - 2015 proficiency	84	6	88	0.54 ± 15 %	0.58 ± 15 %



test exercise

→ 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 ⁶³Ni, ⁵⁵Fe and ⁹⁹Tc in various radwaste.

Hepiegne et al., The separation of ⁹⁹Tc from low and medium-level radioactive wastes and its determination by inductively coupled plasma mass spectrometry, Talanta 41 (1995) 803-809.
 Gautier et al., A comparative study using liquid scintillation counting to determine ⁶³Ni in low and intermediate level radioactive waste, J. Radioanal. Nucl. Chem. 308 (2016) 261-270.
 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.
 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.