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## A comparative study using liquid scintillation counting to determine $^{63}\text{Ni}$ in low and intermediate level radioactive waste

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1     **A comparative study using liquid scintillation counting**  
2             **to determine  $^{63}\text{Ni}$  in low and intermediate level**  
3                     **radioactive waste**

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6     and intermediate level radioactive waste

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14 **A comparative study using liquid scintillation counting**  
15 **to determine  $^{63}\text{Ni}$  in low and intermediate level**  
16 **radioactive waste**

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23 **Abstract**

24 A comparative study using liquid scintillation counting was performed to measure  $^{63}\text{Ni}$  in  
25 low and intermediate level radioactive waste. Three dimethylglyoxime (DMG)-based  
26 radiochemical procedures (solvent extraction, precipitation, extraction chromatography)  
27 were investigated, the solvent extraction method being considered as the reference  
28 method. Theoretical speciation calculations enabled to better understand the chemical  
29 reactions involved in the three protocols and to optimize them. In comparison to the  
30 method based on DMG precipitation, the method based on extraction chromatography  
31 allowed to achieve the best results in one single step in term of recovery yield and  
32 accuracy for various samples.

33 **Keywords**

34  $^{63}\text{Ni}$ , radiochemical analysis, liquid scintillation counting, decommissioning, radioactive  
35 waste, dimethylglyoxime

36        **Introduction**

37        In France, the National Radioactive Waste Management Agency (ANDRA) is in  
38 charge of the long-term management of all radioactive waste. Several repository sites  
39 have been built in order to accommodate nuclear waste packages. One is dedicated to the  
40 Low and Intermediate Level short-lived Waste. The specifications for 143 radionuclides  
41 have been defined by ANDRA which guarantees the safety of the facility [1]. Among this  
42 long list,  $^{63}\text{Ni}$  has to be declared as soon as its activity concentration is over  $1 \text{ Bq g}^{-1}$  and  
43 its maximum acceptance limit has been fixed to  $3 \times 10^6 \text{ Bq g}^{-1}$  [1].  $^{63}\text{Ni}$  is produced by  
44 neutron activation reactions of stable Ni and Cu which are components of various  
45 materials used in the nuclear fuel cycle [2]. Consequently,  $^{63}\text{Ni}$  can be present in many  
46 radioactive materials and waste samples [2-17], such as graphites [6, 7], metals  
47 (aluminium, lead, steel) [6-11], concretes [6, 7, 10, 12], ion-exchange resins and  
48 charcoals [13], effluents [8, 14-17], sludges [14] and environmental samples [10, 18].

49         $^{63}\text{Ni}$  is a long-lived radionuclide with a half-life of 98.70 years ( $\pm 24$ ) [19]. It is a pure  
50 beta emitter with a maximum energy of 66.98 keV [19]. As liquid scintillation counting  
51 (LSC) has a high counting efficiency for  $^{63}\text{Ni}$  (around 70 %) [2], this detection technique  
52 is widely used for  $^{63}\text{Ni}$  determination [2-17]. As a pure beta emitting radionuclide,  $^{63}\text{Ni}$   
53 must be isolated from the matrix and the interfering radionuclides (especially  $^{60}\text{Co}$  a  
54 major radionuclide which has a similar chemical behavior) through chemical separations  
55 prior to any analysis by LSC [2-17]. Consequently, a selective radiochemical method is  
56 needed to measure  $^{63}\text{Ni}$  in low and intermediate level radioactive waste [2-18]. Most  
57 procedures of  $^{63}\text{Ni}$  purification rely on the complexing agent of dimethylglyoxime  
58 (DMG) implemented in three different types of methods: solvent extraction, precipitation  
59 and extraction chromatography [2-18]. In all cases, the  $\text{Ni}(\text{DMG})_2$  complex is favourably  
60 formed at basic pH, around 8-9 [2-18]. The recovery yield of the overall radiochemical  
61 procedure is generally determined from the measurement of stable Ni by atomic  
62 absorption spectroscopy (AAS) [12] or inductively coupled plasma - atomic emission  
63 spectroscopy (ICP-AES) [5, 13, 15, 17].

64 Two or three decades ago, the reference radiochemical method to analyse  $^{63}\text{Ni}$  was  
65 based on a liquid-liquid extraction procedure. The  $\text{Ni}(\text{DMG})_2$  complex is first extracted  
66 in an organic solvent [20], commonly chloroform [8, 10, 11, 18, 20] which has a higher  
67 Ni extraction capacity [20]. Ni is then back-extracted in aqueous solution, mostly with  
68 hydrochloric acid [11, 16, 18]. In France, this extraction method has been standardized in  
69 the standard NF M60-317 to determine  $^{63}\text{Ni}$  in radioactive effluents and waste [21]. Ni  
70 amount is generally less than 1 mg [8, 18, 20] whereas the DMG amount varies from 10  
71 mg [20] to 250 mg [8]. By replicating several extractions, this type of separation  
72 procedure enabled to achieve satisfactory decontamination factors of Co towards Ni (less  
73 than 0.2% of Co was extracted) [8]. In spite of its efficiency, the implementation of this  
74 solvent extraction procedure has tended to decrease in the last decades because of the  
75 restrictions of chloroform use, notably through the European REACH regulation [22].

76 An alternative method to solvent extraction is the precipitation of the  $\text{Ni}(\text{DMG})_2$   
77 complex [4, 9, 12-14]. The French standard NF M60-317 also includes this alternative  
78 option as a second  $^{63}\text{Ni}$  purification method [21]. When the total activity concentrations  
79 of the other radionuclides are 10 times higher in comparison to  $^{63}\text{Ni}$ , this standard  
80 indicates the necessity to perform a second precipitation step [21]. Higher Ni amount is  
81 added (around 2 or 3 mg) [12-14] whereas the DMG amount varies from 50 mg [12, 13]  
82 to 200 mg [21] to favour the precipitation of the  $\text{Ni}(\text{DMG})_2$  complex, in comparison to  
83 the solvent extraction method. Prior to LSC, the precipitate is destroyed to recover  $^{63}\text{Ni}$  in  
84 solution by using concentrated nitric acid [4, 9, 12, 13] or hydrogen peroxide [14]. The  
85 procedure based on  $\text{Ni}(\text{DMG})_2$  precipitation has been applied for the measurement of  
86  $^{63}\text{Ni}$  in various radioactive matrices [4], such as metals [9], concretes [12], ion exchange  
87 resins [13] and sludges [14]. However, the destruction of  $\text{Ni}(\text{DMG})_2$  precipitate appears  
88 to be a delicate and fastidious step before LSC analysis [21].

89 To overcome these above problems, the technique of extraction chromatography  
90 based on the Eichrom  $\text{Ni}^{\text{®}}$  resin has been developed to isolate Ni from the interfering  
91 elements [23]. Some authors also prepared in-house Ni resins which relies on the same  
92 principle [15, 27]. Indeed, over the past 20 decades, extraction chromatography has  
93 become a leading technique for separation and preconcentration of radionuclides in the

94 environmental, biological and nuclear fields [24, 25]. The combination of an organic  
95 extractant coated on an inert support delivers the selectivity of solvent extraction with the  
96 ease of use of resin based methods. In the case of Ni resin, the DMG extractant is coated  
97 on an inert support of acrylic ester based-resin [23]. As relatively high amounts of DMG  
98 and Ni are involved (respectively 50 mg and 2 to 3 mg for a 2 mL pre-packed column  
99 [23]), on-column precipitation of Ni with DMG occurs on Ni resin [23]. Elimination of  
100 the interfering elements is mainly achieved with ammonium citrate during the rinsing  
101 step. Then, Ni is generally stripped from the column using nitric acid [23, 26]. In recent  
102 years, many radiochemical procedures based on Ni resin have been applied on many  
103 nuclear materials [5, 6, 12, 13, 15, 17, 27].

104 DMG is an effective and selective complexing agent of Ni but also of other metal  
105 elements, such as Co, Cu, Cd and Pd [28], which can induce interferences for  $^{63}\text{Ni}$   
106 purification. Indeed, the  $^{60}\text{Co}$  activation product is often present in substantial amounts in  
107 radioactive materials in comparison to  $^{63}\text{Ni}$ . Correlation factors between  $^{63}\text{Ni}$  and  $^{60}\text{Co}$   
108 highly depend on the types of nuclear plants and samples [29]. In CEA France, the third  
109 quartile of  $^{63}\text{Ni}/^{60}\text{Co}$  ratio has been determined at 0.4 in solid radioactive waste.  
110 Consequently, from the literature, it is frequently necessary to complete the purification  
111 step based on DMG with other separation procedures so as to eliminate Co efficiently. In  
112 the French standard NF M60-317, the elimination of Co is achieved with a preliminary  
113 liquid-liquid extraction step based on the use of 2-nitroso-1-naphthol [21]. In this  
114 standard, it is recommended to implement this Co solvent extraction when the total  
115 activity concentrations of the other radionuclides are 10 times higher in comparison to  
116  $^{63}\text{Ni}$  [21]. Furthermore, the presence of  $^{55}\text{Fe}$ , another significant activation product, can  
117 also hinder the formation of  $\text{Ni}(\text{DMG})_2$  complex/precipitate because of its precipitation at  
118 basic pH [23, 26]. Organic complexing agents, such as citric acid [6, 12, 21], tartaric acid  
119 [9, 21] or oxalic acid [5] are generally introduced to prevent the precipitation of Fe and  
120 the other metal elements at basic pH. However, their chelating properties may not be  
121 sufficient in case of high Fe amounts, such as in steels [6, 28]. Consequently, it is also  
122 highly recommended to remove Fe to achieve accurate  $^{63}\text{Ni}$  measurements. Precipitation  
123 with ammonia [12-16, 18] or hydroxide [6, 14] and anion exchange chromatography [4,  
124 5, 9, 10, 11, 14, 15, 17] have been mainly applied in order to eliminate the interfering

125 elements such as Co and Fe. Decontamination factors of  $10^5$  or higher can be obtained  
126 using a combination of these purification methods [2, 6]. In our group, the reference  
127 radiochemical procedure to measure  $^{63}\text{Ni}$  corresponds to the French standard NF M60-  
128 317 [21]. It consists in combining systematically the Co solvent extraction (based on 2-  
129 nitroso-1-naphthol) with the Ni solvent extraction (based on DMG). This method has  
130 been applied to various radioactive waste samples and in particular to graphites [30, 31].  
131 The works reported in the literature generally include several separation steps to analyse  
132  $^{63}\text{Ni}$  [4-18] but do not compare different methods of  $^{63}\text{Ni}$  determination. So, it is not  
133 obvious to choose the most effective and simple procedure for the measurement of  $^{63}\text{Ni}$  in  
134 various low and intermediate level radioactive waste samples.

135 The aim of this work is to propose a reliable radiochemical method to measure  $^{63}\text{Ni}$  in  
136 various low and intermediate level radioactive waste with a large range of  $^{63}\text{Ni}/^{60}\text{Co}$   
137 ratios. For that purpose, the speciation of metal elements (Ni, Co and Fe) is first  
138 discussed so as to achieve a better understanding of their behaviours in the chemical  
139 reactions involved in the different separation steps. Subsequently, three radiochemical  
140 procedures based on the use of DMG complexing agent were applied to different  
141 radioactive samples (evaporate concentrates, steels, muds embedded in concretes,  
142 effluents, ion exchange resins embedded or not in polymers and graphites). Solvent  
143 extraction, precipitation and extraction chromatography based on DMG were compared  
144 in terms of recovery yield and accuracy to determine the radiochemical method the most  
145 selective in one single separation step.

146

## 147 **Experimental**

### 148 **Reagents and equipments**

149 All chemicals (nitric acid, hydrochloric acid, hydrofluoric acid, hydroiodic acid,  
150 ammonium hydroxide, hydrogen peroxide, citrate ammonium, sodium citrate, tartaric  
151 acid, 2-nitroso-1-naphthol, dimethylglyoxime) were of analytical grade. Ultra-pure water

152 (resistivity 18.2 M $\Omega$  cm) was obtained from a Milli-Q purification system (Millipore,  
153 France). Anion-exchange resin AG1-X4 (50-100 mesh) was supplied by Bio-Rad  
154 Laboratories (France). In-house 0.8 cm x 5 cm columns were prepared with 2 g of AG1-  
155 X4 resin. Pre-packed Ni<sup>®</sup> cartridges of 2 mL (100-150 mesh) were purchased from  
156 Triskem International (France).

157 All <sup>63</sup>Ni measurements were performed with a Tri-Carb liquid scintillation counter  
158 (Perkin-Elmer, France). The instrument was calibrated using a certified <sup>63</sup>Ni standard  
159 (NI63ELSB30 having a massic activity of 4 x 10<sup>4</sup> Bq g<sup>-1</sup>  $\pm$  3.5%) which was purchased  
160 from CERCA LEA (France). After the radiochemical procedures, aliquots of 5 mL of the  
161 <sup>63</sup>Ni purified samples were mixed with 15 mL Ultima Gold<sup>™</sup> LLT scintillation cocktail  
162 (Perkin-Elmer, France) in 20 mL polyethylene vials (Perkin-Elmer, France). All  
163 measurements of gamma emitting radionuclides were completed using a high purity  
164 germanium detector (Canberra, France) which was calibrated with a multi gamma  
165 standard (9ML01ELME20) supplied by CERCA LEA (France). Spectral analysis and  
166 quantification were carried out with Genie 2000 software. The accuracy of our  
167 radiological analyses was previously checked with proficiency tests, in particular with the  
168 European Carbowaste project on irradiated graphites [30, 31]. The uncertainties of the  
169 <sup>63</sup>Ni activities concentrations were calculated according to the standard NF M60-317 [21]  
170 by combining the uncertainties associated with the quantities of digested samples, the  
171 standards, the recovery yields and the LSC measurements. The overall expanded  
172 uncertainties were calculated by using a coverage factor k of 2.

173 Stable Fe, Co and Ni concentrations were measured using an ICP-AES (Inductively  
174 Coupled Plasma - Atomic Emission Spectroscopy) Activa M spectrometer (HORIBA  
175 Jobin Yvon, Longjumeau, France). External calibration curves were established from ICP  
176 standards (SPEX Certiprep, USA). The accuracy of our elemental analyses was  
177 previously checked with proficiency tests, in particular those organized by the French  
178 CETAMA and AGLAE committees.

179

180



181        Sample preparation and digestion

182        The different radioactive samples were collected in several French nuclear facilities  
183 and laboratories. They consisted of the following types of materials: evaporate  
184 concentrates, steels, muds embedded in concretes, effluents, ion exchange resins  
185 embedded or not in polymers and graphites (denoted from S1 to S8 in this work). They  
186 were chosen in order to cover a wide range of  $^{63}\text{Ni}/^{60}\text{Co}$  ratios (from 0.3 to 16.4). All  
187 samples were digested using a microwave acid digestion system (Speed Wave, Berghof,  
188 Germany), except graphites. The digestion conditions were consistent with the French  
189 guide NF M60-323 [32]. The evaporate concentrate sample (denoted as S1), the effluent  
190 (denoted as S4) and the ion exchange resins embedded or not in polymers (denoted as S5,  
191 S7 and S8) were digested with 15 mL of concentrated  $\text{HNO}_3$ . The steel sample (denoted  
192 as S2) was digested using aqua regia (5 mL of concentrated  $\text{HNO}_3$  and 10 mL of  
193 concentrated  $\text{HCl}$ ). The muds embedded in concretes (denoted as S3) were digested using  
194 a mixing of 10 mL of concentrated  $\text{HNO}_3$  and 5 mL of concentrated  $\text{HF}$ . The graphite  
195 samples were digested by using  $\text{HI}$  in excess and 5 mL of concentrated  $\text{H}_2\text{SO}_4$  so as to  
196 decompose graphite as  $\text{CO}_2$  by heating. In all cases, 0.2 g up to 5 g of samples were  
197 digested. The resulting solutions were transferred to 100 mL volumetric flasks and  
198 diluted with ultra-pure water. Aliquots were prepared for the determination of stable  
199 metal elements and gamma emitting radionuclides by ICP-AES and gamma  
200 spectrometers respectively. As a function of the  $^{63}\text{Ni}$  activity concentrations, 5 mL to 20  
201 mL of the digested samples were used for  $^{63}\text{Ni}$  purification. The amount of added Ni  
202 carrier was then adapted depending on the studied radiochemical methods (from 0.1 mg  
203 to 4 mg). As examples, the chemical and radiochemical compositions of two studied  
204 samples (S1 and S2) are detailed in Table 1. For S2 steel,  $^{55}\text{Fe}$  activity concentration was  
205 determined at  $7 \times 10^3 \text{ Bq g}^{-1}$  from the French standard NF M60-322 which relies on the  
206 solvent extraction of the Fe complex formed with cupferron (N-nitroso-N-  
207 phenylhydroxylamine) in chloroform [33].

208

209 Radiochemical separation

210 *Method 1 based on the organic extraction of the Ni(DMG)<sub>2</sub> complex*

211 Method 1 is based on the organic extraction of the Ni(DMG)<sub>2</sub> complex. It  
212 corresponds to one of the separation protocols described in the standard NF M60-317  
213 [21]. This is the reference radiochemical procedure of our group to measure <sup>63</sup>Ni in  
214 radioactive waste and effluents [30]. Aliquots of the digested samples were first weighed  
215 in a beaker. 0.1 mg of Ni carrier and 0.5 mg of Co carrier were then added. After the  
216 addition of 5 mL concentrated HNO<sub>3</sub>, the solutions were evaporated to dryness and the  
217 residues were dissolved in a few mL of HNO<sub>3</sub>. 10 mL of sodium citrate (100 g/L) was  
218 then added and the pH of the solutions was adjusted between 3 and 4 with NH<sub>4</sub>OH.  
219 Afterwards, 1 mL of concentrated hydrogen peroxide was added to oxidize Co. Then, 4  
220 mL of an acetic solution of 2-nitroso-1-naphthol (10 g/L) was introduced. As the reaction  
221 between Co and 2-nitroso-1-naphthol proceeds rather slowly [34], the solutions were  
222 allowed to stand for about 30 min. 3x10 mL of chloroform were then added to extract the  
223 Co-nitrosonaphthol complex in the organic phases whereas Ni remained in the aqueous  
224 phases. Thereafter, the pH of the solutions was adjusted to 9 with concentrated NH<sub>4</sub>OH. 2  
225 mL of DMG solution (10 g/L in ethanol) was then added. After a waiting period of 1  
226 hour, 3x10 mL of chloroform were added to extract the Ni(DMG)<sub>2</sub> complex. Afterwards,  
227 the organic phases were washed with 10 mL of 5 % NH<sub>4</sub>OH. Ni was then back-extracted  
228 using 3x10 mL of 0.5 M HCl. The obtained solutions were then evaporated to dryness  
229 and the residues were dissolved in 10 mL of 0.5 M HCl. Finally, a 5 mL aliquot of the  
230 <sup>63</sup>Ni purified samples was prepared for LSC as described above.

231 *Method 2 based on the precipitation of the Ni(DMG)<sub>2</sub> complex*

232 Method 2 is based on the precipitation of the Ni(DMG)<sub>2</sub> complex. It is also described  
233 in the standard NF M60-317 [21]. As the total activity concentrations of the other  
234 radionuclides are not 10 times higher in comparison to <sup>63</sup>Ni in the studied samples, only  
235 one precipitation step was implemented from the specifications of this standard [21].

236 Aliquots of the digested samples were first weighed in a beaker. 10 mL of a saturated  
237 tartaric solution and 4 mg of Ni carrier were then added. The pH of the solutions was  
238 adjusted to 9 with concentrated  $\text{NH}_4\text{OH}$ . 5 mL of DMG solution (1% in ethanol) was then  
239 added. The obtained solutions were heated at  $50^\circ\text{C}$  during 30 min so as to favour the  
240 precipitation of the  $\text{Ni}(\text{DMG})_2$  complex. The precipitates were collected by filtration and  
241 washed with water. Thereafter, Ni was recovered by pouring gently 5 M HCl on the  
242 precipitate. Afterwards, the solutions were evaporated near to dryness (otherwise  
243 insoluble black residues were obtained as indicated in Ref. [26]). DMG was then  
244 decomposed with hydrogen peroxide. Thereafter, the obtained solutions were evaporated  
245 to dryness and the residues were dissolved in 10 mL of 0.5 M HCl. Finally, a 5 mL  
246 aliquot of the  $^{63}\text{Ni}$  purified samples was prepared for LSC as described above.

247 *Method 3 based on the precipitation of the  $\text{Ni}(\text{DMG})_2$  complex on Ni resin*

248 Method 3 is based on the precipitation of the  $\text{Ni}(\text{DMG})_2$  complex on Ni resin [23]. It  
249 corresponds to the radiochemical method described by Eichrom Technologies [26] and  
250 applied in many reported works [6, 12, 13, 15, 17, 27]. Aliquots of the digested samples  
251 were first weighed in a beaker and 2 mg of Ni carrier were then added. After the addition  
252 of 5 mL concentrated HCl, the solutions were evaporated to dryness and the residues  
253 were dissolved in a few mL of 1 M HCl. 1 mL of 1 M ammonium citrate (that was  
254 preliminary adjusted to pH 8-9 with  $\text{NH}_4\text{OH}$ ) was then added. Afterwards, the pH of the  
255 solutions was adjusted between 8 and 9 with  $\text{NH}_4\text{OH}$ . The samples were then loaded on  
256 the prepared Ni columns. The pre-packed Ni columns were preliminary conditioned with  
257 20 mL of 0.2 M ammonium citrate that was adjusted to pH 8-9 with  $\text{NH}_4\text{OH}$ . After the  
258 loading of the samples, the Ni columns were rinsed with 20 mL of 0.2 M ammonium  
259 citrate (that was adjusted to pH 8-9 with  $\text{NH}_4\text{OH}$ ) to eliminate the interfering elements.  
260 Thereafter, Ni was stripped with 5 mL of 3 M  $\text{HNO}_3$ . Finally, a 5 mL aliquot of the  $^{63}\text{Ni}$   
261 purified samples was prepared for LSC as described above. In those conditions, our  
262 group checked that the presence of 3 M  $\text{HNO}_3$  and DMG did not induce any quenching  
263 effect in LSC by performing the protocol with a  $^{63}\text{Ni}$  standard. Eichrom Technologies  
264 recommend to eliminate Fe prior to the separation on Ni column [26] but no threshold of

265 Fe concentration is indicated. Given the Fe compositions of the studied samples, an  
266 additional purification step was introduced only for the steel sample. From the works of  
267 Hou et al. and Rajkovich et al. [6, 23], it was decided to implement a separation on the  
268 anion exchange AG1-X4 resin before the purification step on the Ni resin. The AG1-X4  
269 resin has indeed a higher loading capacity towards Fe (around 15 mg/g resin) in  
270 comparison to TRU resin (5 mg/g resin). In concentrated HCl, Co and Fe are fixed on the  
271 anion exchange resin whereas Ni is not retained [4, 5, 6, 13, 15-17]. In the case of steels,  
272 2 mg of Ni carrier and 1 mg of Co carrier were added to the aliquots of the digested  
273 samples. The solutions were evaporated to dryness and the residues were dissolved in 5  
274 mL of 8 M HCl. The samples were then loaded on the AG1-X4 columns which were  
275 preliminary conditioned with 25 mL of 8 M HCl. After the loading of the samples, Ni  
276 was eluted with 5 mL of 8 M HCl. The resulting solutions were then evaporated to  
277 dryness and the residues were treated as described above in the protocol dedicated to the  
278 Ni columns.

279

## 280 **Results and discussion**

### 281 *Speciation studies*

282 A previous work of our group demonstrated the importance of speciation studies in  
283 order to achieve a better understanding of the behaviours of the analytes during the  
284 different separation steps and to optimize the radiochemical procedures [25]. This  
285 approach was also investigated by Roskopfova et al. so as to determine the Ni species in  
286 a method dedicated to  $^{63}\text{Ni}$  purification in nuclear waste [12]. Nonetheless, Roskopfova  
287 et al. did not take into account of all the chemical reagents (such as citrate) and the  
288 interfering elements (such as Co and Fe) in their speciation calculations [12], which can  
289 influence greatly the speciation results. Indeed, as a pure beta emitter,  $^{63}\text{Ni}$  needs to be  
290 isolated from the matrix and the interfering elements. Consequently, speciation studies  
291 were performed by considering the main chemicals and metal elements involved in the

292 three  $^{63}\text{Ni}$  radiochemical methods studied by our group. For that purpose, speciation  
293 calculations were made with JChess software (Ecole des Mines ParisTech, France). The  
294 database of the software (chess.tdb) was enriched with specific stability constants of Ni,  
295 Co and Fe with ammonia, citrate, tartrate and DMG (the stability constants related to  
296 hydroxide complexes and precipitates were already included). The relevant stability  
297 constants were obtained from Smith and Martell [28]. As citric acid has three acidic  
298 functions (the corresponding pKa values are: pKa1 = 3.1, pKa2 = 4.8, pKa3 = 6.4) [28], it  
299 was denoted as  $\text{H}_3\text{Cit}$ . In the same way, tartaric acid was denoted as  $\text{H}_2\text{Tart}$  (the  
300 corresponding pKa values are: pKa1 = 2.7, pKa2 = 3.7) [28]. Simple calculations were  
301 first performed by investigating the behaviours of Ni, Co and Fe in NaOH and  $\text{NH}_4\text{OH}$ .  
302 Whatever their quantities, Ni, Co and Fe are predicted to precipitate quantitatively with  
303 hydroxide ions by using NaOH. Fe is foreseen to precipitate and can also co-precipitate  
304 avec Co in  $\text{NH}_4\text{OH}$  medium, depending on their quantities. With regard to Ni, its  
305 predominant species are  $\text{Ni}(\text{NH}_3)_x^{2+}$  complexes by using  $\text{NH}_4\text{OH}$ : no significant Ni  
306 precipitation is predicted at basic pH. Those results were in agreement with the  
307 experimental studies of Hou et al. [6], which proves the reliability of our JChess  
308 calculations.

309 The results obtained from JChess software are presented for the S2 steel sample (its  
310 chemical composition is given in Table 1) but similar conclusions can be drawn for the  
311 other materials, such as the S1 evaporate concentrate. The theoretical distribution  
312 diagrams of Ni(II), Co(II) and Fe(III) species are depicted respectively in Figures 1 to 3  
313 for method 1. In the case of method 1, after the treatment of the sample in  $\text{HNO}_3$ ,  
314 sodium citrate was added and pH was adjusted to 3-4 with  $\text{NH}_4\text{OH}$ . From JChess  
315 calculations, the predominant Ni(II) species are  $\text{Ni}^{2+}$ ,  $\text{Ni}(\text{NO}_3)^+$  and Ni-citrate complexes  
316 ( $\text{NiCit}^-$  and  $\text{NiH}_2\text{Cit}^+$ ) at pH 3-4. Those results are consistent with the work of Zelenin et  
317 al. who investigated the interaction of the Ni(II) ion with citric acid in an aqueous  
318 solution [35]. It is predicted that Co has the same behaviour as Ni at pH 3-4: the  
319 predominant Co(II) species are  $\text{Co}^{2+}$ ,  $\text{Co}(\text{NO}_3)^+$  and Co-citrate complexes ( $\text{CoCit}^-$  and  
320  $\text{CoH}_2\text{Cit}^+$ ). In those pH conditions, the predominant Fe(III) species are Fe-citrate  
321 complexes ( $\text{FeCit}$  and  $\text{FeOHCit}^-$ ). For method 1, no precipitation is predicted at pH 3-4.  
322 Consequently, after the addition of hydrogen peroxide, Co can be complexed by 2-

323 nitroso-1-naphthol and further extracted by chloroform [34], which induces an efficient  
324 elimination of Co. From literature [34], Fe can also be partly extracted. In this step, Ni  
325 which was not complexed by 2-nitroso-1-naphthol remained in the aqueous phase. The  
326 pH of the aqueous solution was then adjusted to 9 with ammonia. The speciation studies  
327 indicate that the predominant Ni(II) species are  $\text{Ni}(\text{NH}_3)_x^{2+}$  complexes at pH 9, which  
328 prevents Ni from precipitating at basic pH. This is not the case for Fe which might start  
329 precipitating as  $\text{Fe}_2\text{O}_3$  hematite when the pH is higher than 6. After the pH adjustment at  
330 9, DMG was added. It can be noted that no stability constant was found for Fe with  
331 DMG: no stable complex might be formed [28]. On the contrary, the predominant Ni(II)  
332 species is the  $\text{Ni}(\text{DMG})_2$  complex at pH 9, which is in agreement with Dyrssen et al. [36].  
333 Consequently, only Ni can be extracted in the organic phase after the addition of  
334 chloroform, which enables a selective purification of Ni for method 1. However, the  
335 presence of Fe precipitate might hinder the Ni extraction and induce a slight decrease of  
336 Ni recovery yield. Finally, Ni can be back-extracted at low pH in HCl medium for LSC  
337 analysis.

338 Concerning method 2, after the addition of tartaric acid and the pH adjustment with  
339 ammonia, the same Ni(II) species as above might be observed: the  $\text{Ni}(\text{NH}_3)_x^{2+}$  complexes  
340 are predicted to be predominant at pH 8-9. In contrast, despite the use of tartaric acid, Co  
341 and Fe are foreseen to precipitate as  $\text{CoFe}_2\text{O}_4$  and  $\text{Fe}_2\text{O}_3$  at basic pH. The complexing  
342 properties of this chelating agent are not sufficient to prevent Co and Fe precipitation in  
343 the case of steels (the formation constant of  $\text{Fe}_2\text{O}_3$  hematite is much greater than the one  
344 of  $\text{FeTart}^+$  [28]). Afterwards, DMG was introduced in the aqueous solution. Since high  
345 amounts of Ni and DMG were used for method 2, the  $\text{Ni}(\text{DMG})_2$  precipitate is predicted  
346 to be formed. As Co and Fe are present as precipitates in the former step, a co-  
347 precipitation with  $\text{Ni}(\text{DMG})_2$  might occur. From speciation calculations, the main  
348 interfering elements, Co and Fe, are predicted to be not eliminated efficiently with  
349 method 2 in the case of a steel sample. Similar results were obtained for the other  
350 samples depending on Co and Fe quantities. It can be noticed that this point was not  
351 precisely specified in the French standard [21]. After the DMG precipitation step, the  
352 precipitate can be dissolved at low pH in concentrated HCl to recover Ni in solution.

353 The distribution diagrams of Ni(II), Co(II) and Fe(III) species related to method 3 are  
354 very close to those obtained for method 1 (see Figures 1 to 3). After the addition of  
355 ammonium citrate and the pH adjustment with ammonia, the predominant Ni(II) species  
356 are  $\text{Ni}(\text{NH}_3)_x^{2+}$  complexes at pH 8-9. As the used quantity of citrate is quite low in  
357 method 3, at pH 8-9, Co and Fe exist as precipitate of  $\text{CoFe}_2\text{O}_4$  and  $\text{Fe}_2\text{O}_3$  in the case of  
358 steel sample. Similar conclusions were obtained for the other samples. Consequently,  
359 cautiousness has to be taken towards method 3 when Co or Fe are present in the analysed  
360 aliquots, which is in agreement with Eichrom Technologies' recommendations [26].  
361 After the pH adjustment, the sample was loaded on the Ni resin which was preliminary  
362 conditioned with ammonium citrate at pH 8-9. Since high amounts of Ni and DMG are  
363 used for method 3, the  $\text{Ni}(\text{DMG})_2$  precipitate is predicted to be formed on the Ni column.  
364 After the rinsing step of the Ni column, concentrated  $\text{HNO}_3$  was introduced. At pH lower  
365 than 1, the predominant Ni(II) species is predicted to be  $\text{Ni}^{2+}$  which allowed the Ni  
366 stripping from the column and its further LSC measurement.

367 From the speciation studies, it can be inferred that the behaviours of Ni, Co and Fe  
368 strongly depend on the considered purification methods. For method 1, no significant  
369 reaction was predicted to hinder the selective isolation of Ni from Co and Fe. On the  
370 contrary, Co and Fe might precipitate quantitatively during the different steps of method  
371 2 and 3 as a function of their concentrations, but these interfering reactions are predicted  
372 to be more pronounced for method 2. For a steel sample, according to JChess  
373 calculations, the quantity of the complexing agent (citrate or tartrate) should be increased  
374 by a 100 fold factor to prevent any Co and Fe precipitation, which is not convenient in  
375 practice. As a consequence, it might be quite difficult to avoid the presence of  
376 interferences for  $^{63}\text{Ni}$  purification by applying only method 2, in case of high amounts of  
377 Co and Fe in the samples.

378

379

380        *Applications of the three DMG-based radiochemical methods to real*  
381 *nuclear waste samples*

382        From the literature, it is not obvious to choose the best selective radiochemical  
383 procedure based on DMG (solvent extraction, precipitation and extraction  
384 chromatography) and to determine if a single separation step can be implemented for  
385 nuclear waste samples. For instance, for method 3 based on Ni column, Rajkovich et al.  
386 [23] reported a decontamination factor of 100000 for Co. On the other hand, Hou et al.  
387 [5] obtained a decontamination factor of 2000 for Co whereas Warwick et al. [15]  
388 indicated the presence of 5 % of Co in the Ni purified fractions. To answer this question,  
389 the three radiochemical methods based on the use of DMG complexing agent were  
390 applied to different types of radioactive waste samples (evaporate concentrates, steels,  
391 muds embedded in concretes, effluents, ion exchange resins embedded or not in polymers  
392 and graphites). The samples denoted from S1 to S8 were chosen so as to cover a large  
393 range of  $^{63}\text{Ni}/^{60}\text{Co}$  ratios from 0.3 to 16.4. In those conditions, less than 2 % of Co must  
394 be present in the Ni purified fractions so that Co does not induce any interference in LSC  
395 analysis.

396        The results obtained for the three DMG-based radiochemical methods are given in  
397 Table 2 in terms of  $^{60}\text{Co}$  and  $^{63}\text{Ni}$  activity concentrations. It can be noted that a wide  
398 range of  $^{63}\text{Ni}$  activity concentrations were measured from 1 to  $2 \times 10^6 \text{ Bq g}^{-1}$  in the eight  
399 samples. For all the studied radioactive waste, the  $^{63}\text{Ni}$  values were lower than the  
400 maximum acceptance limit fixed by ANDRA at  $3 \times 10^6 \text{ Bq g}^{-1}$  [1].

401        The three DMG-based radiochemical procedures were compared in terms of Ni  
402 recovery yields in Figure 4. The Ni recovery yields were satisfactory whatever the  
403 analysed samples and the radiochemical methods. Those results are in agreement with the  
404 values reported in the literature [4-18]. For method 1 based on solvent extraction, it can  
405 be noticed that the Ni recovery yields varied from 69 % to 97 %. The lower value of Ni  
406 recovery yield was obtained for the steel sample purified with method 1. This could be  
407 explained by the Fe precipitation which might hinder slightly the extraction of  $\text{Ni}(\text{DMG})_2$



408 complex in the organic phase at pH 9, in agreement with the theoretical speciation  
409 calculations. Whatever the sample, the values of Ni recovery yields were higher than 95  
410 % and 90 % respectively for methods 2 and 3.

411 The three DMG-based radiochemical methods were then compared in terms of  
412 normalized errors in Figure 5, the method 1 based on solvent extraction being considered  
413 as the reference method. The formula used for calculating the normalized error E-normal  
414 (denoted as  $E_n$ ) is shown in Equation 1 [37]. When  $E_n$  is lower than 1, the performances  
415 of the studied method are judged as satisfactory.

$$416 \quad E_n = \frac{|x_i - X_{\text{method 1}}|}{\sqrt{\left( U_i^2 + U_{\text{method 1}}^2 \right)}} \quad \text{Eq. (1)}$$

417 Where

418  $x_i$  is the  $^{63}\text{Ni}$  measurement result obtained with method  $i$  ( $i=2$  to  $3$ )

419  $X_{\text{method 1}}$  is the  $^{63}\text{Ni}$  reference measurement result obtained with method 1

420  $U_i$  is the expanded uncertainty of  $x_i$

421  $U_{\text{method 1}}$  is the expanded uncertainty of  $X_{\text{method 1}}$ .

422 For method 2 based on DMG precipitation, the  $E_n$  values were higher than 1 for the  
423 majority of the studied samples (up to 17), which indicated that the performances of  
424 method 2 were unsatisfactory. For instance, the  $E_n$  value related to the S2 steel was  
425 around 2. In agreement with the theoretical speciation calculations, those unacceptable  
426 results might be related to the presence of Fe and Co in the Ni purified fractions due to  
427 their precipitations at basic pH. This hypothesis was confirmed by gamma and ICP-AES  
428 measurements. Around 2 % of Fe (thus  $^{55}\text{Fe}$ ) and 2 % of  $^{60}\text{Co}$  were respectively  
429 determined in the Ni fractions, which induced interferences for  $^{63}\text{Ni}$  characterization by  
430 LSC, given the  $^{63}\text{Ni}/(^{60}\text{Co}+^{55}\text{Fe})$  ratio of 0.2 and  $^{63}\text{Ni}/^{60}\text{Co}$  ratio of 0.4 in the S2 steel. As  
431 a conclusion, method 2 implemented with a single precipitation step was not selective  
432 enough to ensure accurate  $^{63}\text{Ni}$  measurements in nuclear waste having a large range of  
433 activity concentrations of interfering elements. Besides, the French standard NF M60-317  
434 prescribes that one DMG-based precipitation step should be sufficient when the total

435 activity concentrations of the other radionuclides are not 10 times higher in comparison  
436 in comparison to  $^{63}\text{Ni}$  [21], which is not in agreement with our experimental results. This  
437 standard published in 2001 [21] might be no more adapted to the nuclear waste produced  
438 in the past decade from decommissioning operations of various radioactive facilities.  
439 Consequently, the French standard NF M60-317 might be revised to take into account of  
440 the variety of the present nuclear waste samples. Co and Fe elimination should be  
441 specified by performing a second systematic purification step which can be a second  
442 DMG-precipitation or a preliminary separation on an anion exchange resin in HCl  
443 medium.

444 For method 3 based on Ni column, the  $E_n$  values were lower than 1 whatever the  
445 studied samples, which demonstrated that the performances of method 3 were  
446 satisfactory. Method 3 proved to be very efficient towards a large variety of radioactive  
447 waste. In conclusion, method 3 implemented in only one single Ni column step was  
448 selective enough to obtain accurate  $^{63}\text{Ni}$  analyses in nuclear waste with various  $^{63}\text{Ni}/^{60}\text{Co}$   
449 ratios, except samples with high Fe contents such as steels. In the case of steels, a  
450 preliminary separation on an anion exchange resin was implemented prior to the Ni resin,  
451 which provided reliable  $^{63}\text{Ni}$  measurements (the  $E_n$  value was 0.6). Indeed, less than 2 %  
452 of Fe (thus  $^{55}\text{Fe}$ ) and 2 % of  $^{60}\text{Co}$  were respectively measured in the Ni fractions.  
453 Consequently, from these studies, method 3 was deduced to be more selective than  
454 method 2 in the case of a single separation step.

455 A systematic separation on an anion exchange resin might be proposed prior to the Ni  
456 resin in order to obtain a simple and reliable radiochemical method that can be applied to  
457 all nuclear matrices whatever their  $^{63}\text{Ni}/^{60}\text{Co}$  ratios and their Fe amounts. To check this  
458 assumption, the S3 sample (corresponding to muds embedded in concrete) was analysed  
459 with and without performing the AG1-X4 separation before the purification of the Ni  
460 column. The difference between the two  $^{63}\text{Ni}$  values was less than 1 % and the values of  
461 Ni recovery yields were very similar (higher than 90 %). Furthermore, a blank separation  
462 was implemented so as to determine the  $^{63}\text{Ni}$  detection limit of the overall method 3. The  
463  $^{63}\text{Ni}$  detection limit was found to be  $0.2 \text{ Bq g}^{-1}$  for an effluent sample, which is  
464 compatible with the  $^{63}\text{Ni}$  declaration threshold fixed by ANDRA at  $1 \text{ Bq g}^{-1}$ . As a

465 conclusion, method 3 based on the AG1-X4 and Ni resins was selected to determine  $^{63}\text{Ni}$   
466 accurately in low and intermediate radioactive waste whatever their chemical and  
467 radiological compositions. In the future, this method which prevents the use of  
468 chloroform might be included in the revised version of the French standard NF M60-317.

469

## 470 **Conclusions**

471  $^{63}\text{Ni}$  is a major activation product which has to be characterized in low and  
472 intermediate level radioactive waste. As a pure beta emitter, this radionuclide must be  
473 isolated from the matrix and the interfering elements (mainly  $^{60}\text{Co}$  and  $^{55}\text{Fe}$ ) through  
474 separation procedures prior to LSC measurement. A comparative study using LSC was  
475 performed to measure  $^{63}\text{Ni}$  in various radioactive waste samples with a large range of  
476  $^{63}\text{Ni}/^{60}\text{Co}$  ratios. Three dimethylglyoxime (DMG)-based radiochemical procedures  
477 (solvent extraction, precipitation, extraction chromatography) were investigated, the  
478 solvent extraction method being considered as the reference method. Theoretical  
479 speciation calculations enabled to better understand the chemical reactions involved in  
480 the different steps of the three protocols and to optimize them. The presence of  
481 significant cobalt and iron quantities was predicted to generate interferences for the  
482 method based on DMG precipitation, in agreement with the experimental results. The  
483 three DMG-based methods were compared in terms of recovery yield and accuracy. In  
484 comparison to the method based on DMG precipitation, the method based on nickel  
485 extraction chromatography resin allowed to achieve the most reliable results in one single  
486 step for the majority of radioactive waste. For the characterization of  $^{63}\text{Ni}$  in all nuclear  
487 waste samples, the combination of a separation on an anion exchange resin and a  
488 purification on a Ni resin was proved to be selective enough to ensure accurate results.  
489 The methodology implemented in this work (based on speciation calculations and  
490 experimental results) can be applied to future developments of radiochemical procedures,  
491 such as  $^{55}\text{Fe}$  determination in nuclear waste.

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592 **Table 1** Chemical and radiochemical compositions of studied nuclear waste samples

	Activity concentration ( $^{60}\text{Co}$ ) ( $\text{Bq g}^{-1}$ )	Activity concentration ( $^{137}\text{Cs}$ ) ( $\text{Bq g}^{-1}$ )	Fe ( $\text{mg g}^{-1}$ )	Co ( $\text{mg g}^{-1}$ )	Ni ( $\text{mg g}^{-1}$ )
Evaporate concentrate S1	$8.64 \times 10^2 \pm 10\%$	$1.66 \times 10^3 \pm 6\%$	$0.4 \pm 10\%$	$< 0.05$	$0.4 \pm 10\%$
Steel S2	$1.10 \times 10^4 \pm 4\%$	$9.88 \times 10^2 \pm 10\%$	$970 \pm 5\%$	$0.2 \pm 10\%$	$6 \pm 10\%$

593

594 **Table 2** Comparison of the three studied DMG-based radiochemical methods in terms of  
 595  $^{60}\text{Co}$  and  $^{63}\text{Ni}$  activity concentrations (n/a\*: not available, \*\* an anion exchange resin is  
 596 implemented prior to Ni column)

	Activity concentration ( $^{60}\text{Co}$ ) ( $\text{Bq g}^{-1}$ )	Activity concentration ( $^{63}\text{Ni}$ ) ( $\text{Bq g}^{-1}$ )			Ratio $^{63}\text{Ni}/^{60}\text{Co}$ for method 1
		Method 1 based on DMG solvent extraction	Method 2 based on DMG precipitation	Method 3 based on Ni column	
Evaporate concentrate S1	$8.64 \times 10^2 \pm 10\%$	$2.76 \times 10^2 \pm 5\%$	$2.50 \times 10^2 \pm 5\%$	$2.88 \times 10^2 \pm 5\%$	0.3
Steel S2	$1.10 \times 10^4 \pm 4\%$	$3.99 \times 10^3 \pm 5\%$	$3.37 \times 10^3 \pm 5\%$	$3.82 \times 10^3 \pm 5\%$ **	0.4
Muds embedded in concrete S3	$1.38 \times 10^4 \pm 4\%$	$8.94 \times 10^3 \pm 5\%$	n/a*	$9.35 \times 10^3 \pm 5\%$	0.7
Effluent S4	$2.10 \pm 10\%$	$1.39 \pm 9\%$	$1.18 \times 10^1 \pm 5\%$	$1.45 \pm 9\%$	0.7
Ion exchange resins S5	$6.65 \times 10^5 \pm 4\%$	$1.81 \times 10^6 \pm 4\%$	$1.76 \times 10^6 \pm 4\%$	$1.73 \times 10^6 \pm 4\%$	2.7
Graphite S6	$4.05 \times 10^3 \pm 4\%$	$2.78 \times 10^4 \pm 4\%$	n/a*	$2.90 \times 10^4 \pm 4\%$	6.9
Ion exchange resins embedded in polymer S7	$2.85 \times 10^4 \pm 4\%$	$3.48 \times 10^5 \pm 4\%$	$3.26 \times 10^5 \pm 4\%$	$3.50 \times 10^5 \pm 4\%$	12.3
Ion exchange resins S8	$4.67 \times 10^3 \pm 4\%$	$7.66 \times 10^4 \pm 4\%$	$6.57 \times 10^4 \pm 4\%$	$7.95 \times 10^4 \pm 4\%$	16.4

597

598



599 **Fig. 1** Theoretical distribution diagram of Ni(II) species for a steel (using JChess  
600 software)

601 **Fig. 2** Theoretical distribution diagram of Co(II) species for a steel (using JChess  
602 software)

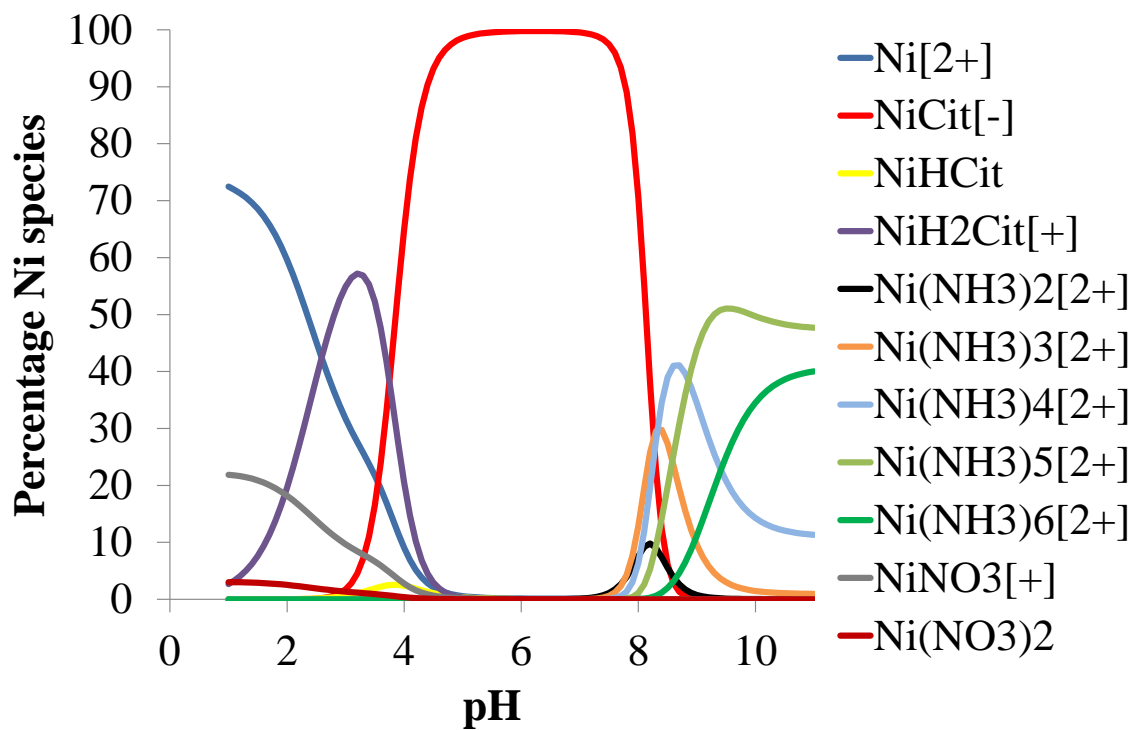
603 **Fig. 3** Theoretical distribution diagram of Fe(III) species for a steel (using JChess  
604 software)

605 **Fig. 4** Ni recovery yields (%) obtained for the three studied DMG-based radiochemical  
606 methods

607 **Fig. 5** Comparison of the studied DMG-based radiochemical methods in terms of  
608 normalized errors  $E_n$

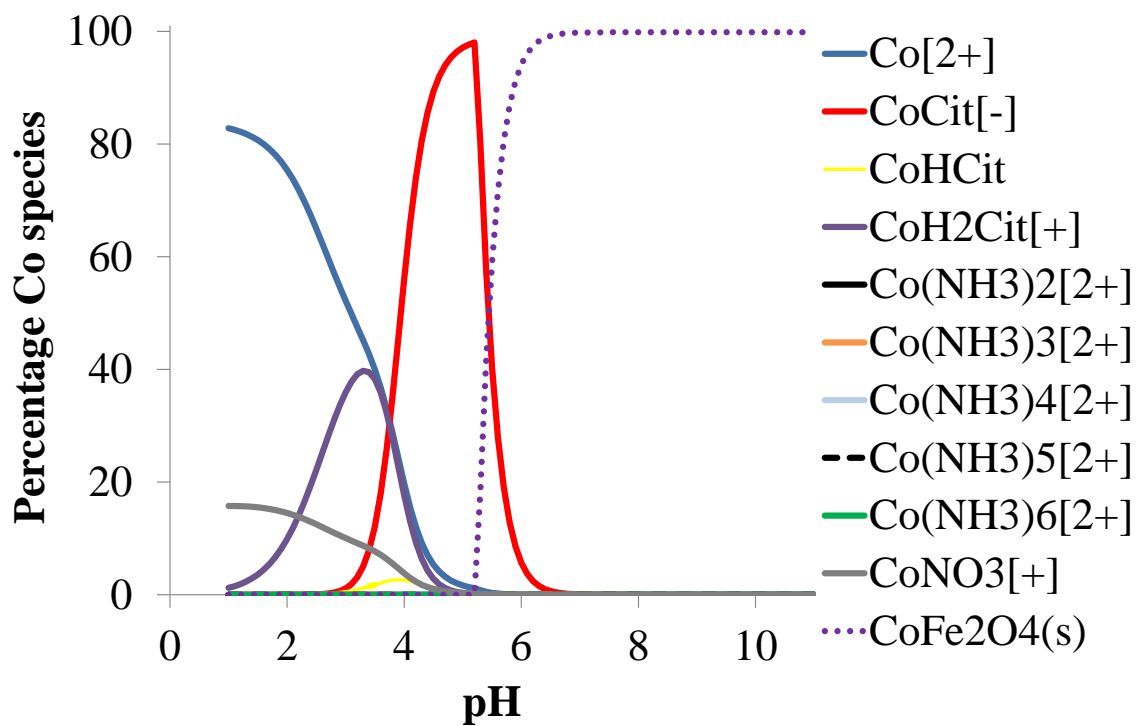
609

610 **Fig. 1** Theoretical distribution diagram of Ni(II) species for a steel (using JChess  
611 software)



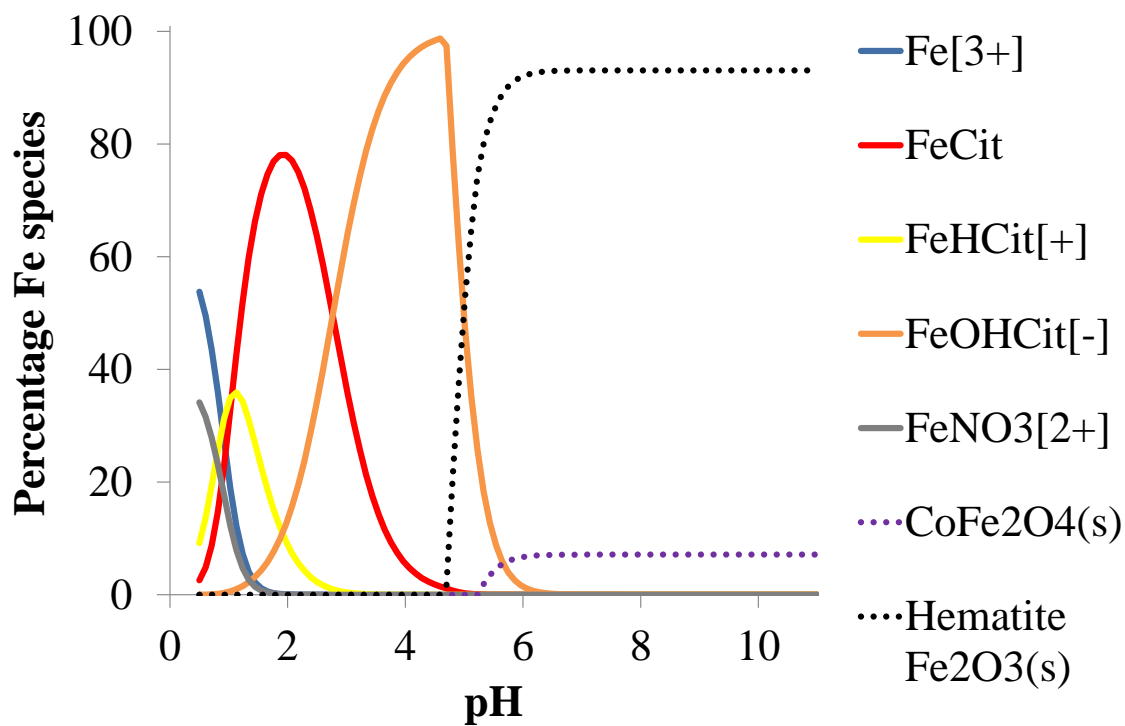
612

613 **Fig. 2** Theoretical distribution diagram of Co(II) species for a steel (using JChess  
614 software)



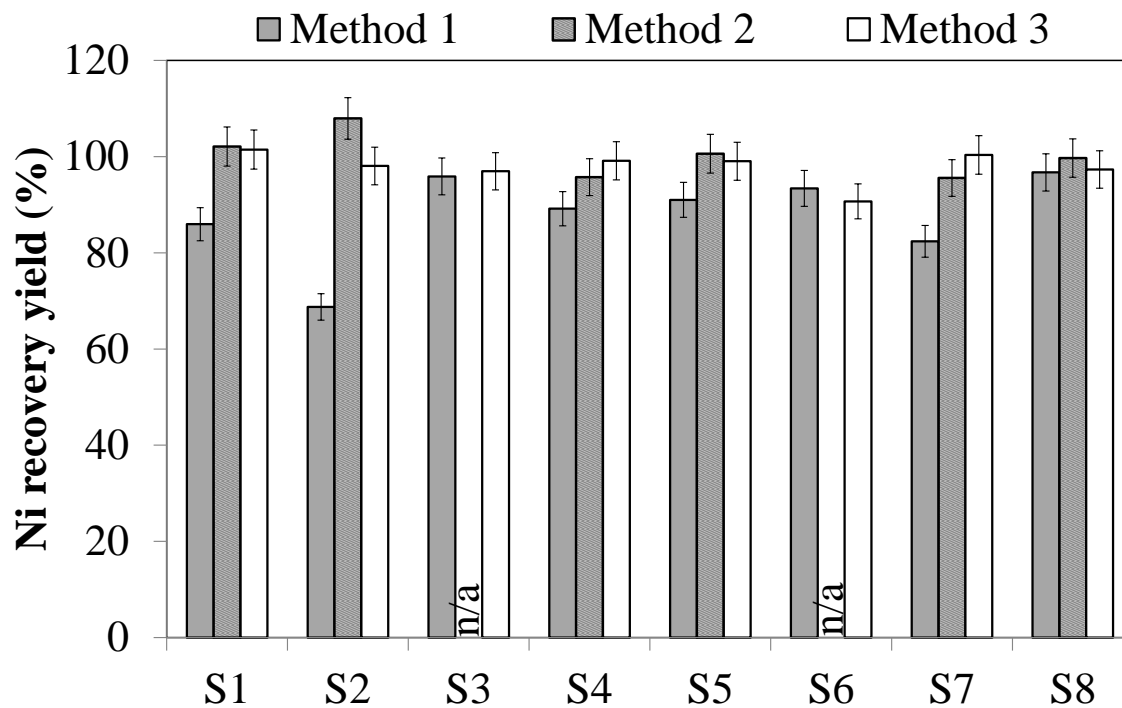
615

616 **Fig. 3** Theoretical distribution diagram of Fe(III) species for a steel (using JChess  
617 software)



618

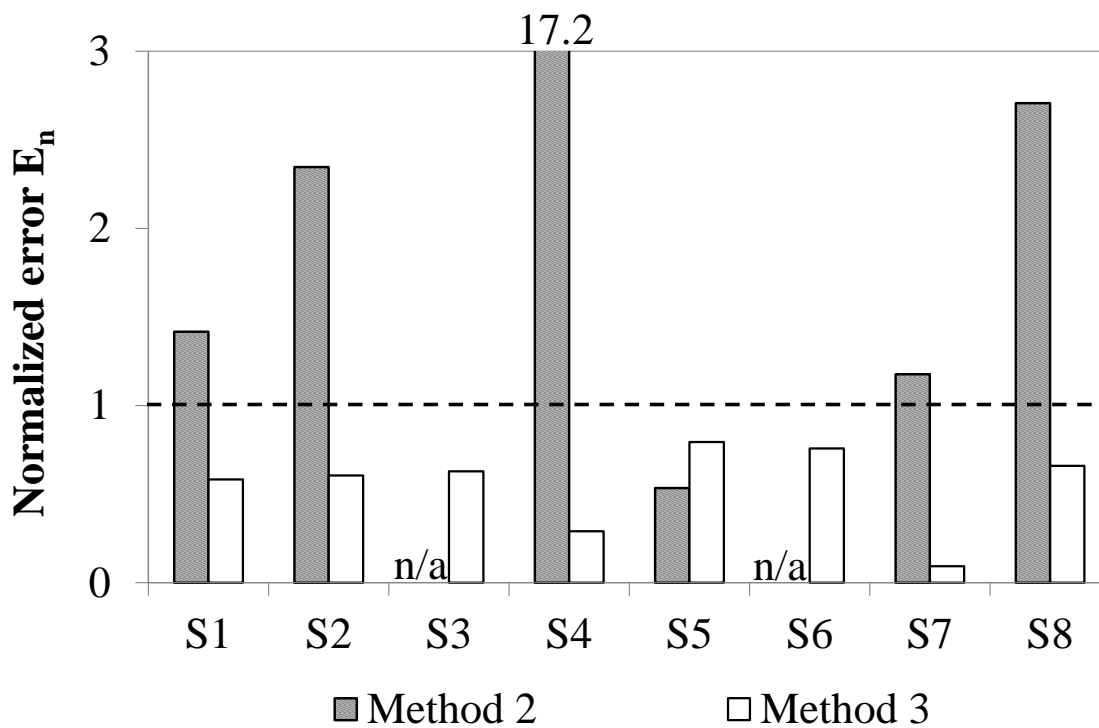
619 **Fig. 4** Ni recovery yields (%) obtained for the three studied DMG-based radiochemical  
620 methods (n/a: not available)



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622

623 **Fig. 5** Comparison of the studied DMG-based radiochemical methods in terms of  
624 normalized errors  $E_n$  (n/a: not available)



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