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To cite this version:

Céline Gautier, Christèle Colin, Cécile Garcia. A comparative study using liquid scintillation counting to determine ^{63}Ni in low and intermediate level radioactive waste. Journal of Radioanalytical and Nuclear Chemistry, 2016, 308 (1), pp.261-270. 10.1007/s10967-015-4301-4 . cea-02383960

HAL Id: cea-02383960

https://cea.hal.science/cea-02383960

Submitted on 28 Nov 2019

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

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Abstract

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

Keywords

^{63}Ni, radiochemical analysis, liquid scintillation counting, decommissioning, radioactive waste, dimethylglyoxime

Introduction

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

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

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

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

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

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

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

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

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

Experimental

Reagents and equipments

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

(resistivity 18.2 MΩ cm) was obtained from a Milli-Q purification system (Millipore, France). Anion-exchange resin AG1-X4 (50-100 mesh) was supplied by Bio-Rad Laboratories (France). In-house 0.8 cm x 5 cm columns were prepared with 2 g of AG1-X4 resin. Pre-packed Ni® cartridges of 2 mL (100-150 mesh) were purchased from Triskem International (France).

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

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

Sample preparation and digestion

The different radioactive samples were collected in several French nuclear facilities and laboratories. They consisted of the following types of materials: evaporate concentrates, steels, muds embedded in concretes, effluents, ion exchange resins embedded or not in polymers and graphites (denoted from S1 to S8 in this work). They were chosen in order to cover a wide range of $^{63}Ni/^{60}Co$ ratios (from 0.3 to 16.4). All samples were digested using a microwave acid digestion system (Speed Wave, Berghof, Germany), except graphites. The digestion conditions were consistent with the French guide NF M60-323 [32]. The evaporate concentrate sample (denoted as S1), the effluent (denoted as S4) and the ion exchange resins embedded or not in polymers (denoted as S5, S7 and S8) were digested with 15 mL of concentrated HNO_3. The steel sample (denoted as S2) was digested using aqua regia (5 mL of concentrated HNO_3 and 10 mL of concentrated HCl). The muds embedded in concretes (denoted as S3) were digested using a mixing of 10 mL of concentrated HNO_3 and 5 mL of concentrated HF. The graphite samples were digested by using HI in excess and 5 mL of concentrated H_2SO_4 so as to decompose graphite as CO_2 by heating. In all cases, 0.2 g up to 5 g of samples were digested. The resulting solutions were transferred to 100 mL volumetric flasks and diluted with ultra-pure water. Aliquots were prepared for the determination of stable metal elements and gamma emitting radionuclides by ICP-AES and gamma spectrometers respectively. As a function of the ^{63}Ni activity concentrations, 5 mL to 20 mL of the digested samples were used for ^{63}Ni purification. The amount of added Ni carrier was then adapted depending on the studied radiochemical methods (from 0.1 mg to 4 mg). As examples, the chemical and radiochemical compositions of two studied samples (S1 and S2) are detailed in Table 1. For S2 steel, ^{55}Fe activity concentration was determined at 7 x 10^3 Bq g^{-1} from the French standard NF M60-322 which relies on the solvent extraction of the Fe complex formed with cupferron (N-nitroso-N-phenylhydroxylamine) in chloroform [33].

Radiochemical separation

Method 1 based on the organic extraction of the $Ni(DMG)_2$ complex

Method 1 is based on the organic extraction of the $Ni(DMG)_2$ complex. It corresponds to one of the separation protocols described in the standard NF M60-317 [21]. This is the reference radiochemical procedure of our group to measure ^{63}Ni in radioactive waste and effluents [30]. Aliquots of the digested samples were first weighed in a beaker. 0.1 mg of Ni carrier and 0.5 mg of Co carrier were then added. After the addition of 5 mL concentrated HNO_3, the solutions were evaporated to dryness and the residues were dissolved in a few mL of HNO_3. 10 mL of sodium citrate (100 g/L) was then added and the pH of the solutions was adjusted between 3 and 4 with NH_4OH. Afterwards, 1 mL of concentrated hydrogen peroxide was added to oxidize Co. Then, 4 mL of an acetic solution of 2-nitroso-1-naphthol (10 g/L) was introduced. As the reaction between Co and 2-nitroso-1-naphthol proceeds rather slowly [34], the solutions were allowed to stand for about 30 min. 3x10 mL of chloroform were then added to extract the Co-nitrosonaphtol complex in the organic phases whereas Ni remained in the aqueous phases. Thereafter, the pH of the solutions was adjusted to 9 with concentrated NH_4OH. 2 mL of DMG solution (10 g/L in ethanol) was then added. After a waiting period of 1 hour, 3x10 mL of chloroform were added to extract the $Ni(DMG)_2$ complex. Afterwards, the organic phases were washed with 10 mL of 5 % NH_4OH. Ni was then back-extracted using 3x10 mL of 0.5 M HCl. The obtained solutions were then evaporated to dryness and the residues were dissolved in 10 mL of 0.5 M HCl. Finally, a 5 mL aliquot of the ^{63}Ni purified samples was prepared for LSC as described above.

Method 2 based on the precipitation of the $Ni(DMG)_2$ complex

Method 2 is based on the precipitation of the $Ni(DMG)_2$ complex. It is also described in the standard NF M60-317 [21]. As the total activity concentrations of the other radionuclides are not 10 times higher in comparison to ^{63}Ni in the studied samples, only one precipitation step was implemented from the specifications of this standard [21].

Aliquots of the digested samples were first weighed in a beaker. 10 mL of a saturated tartaric solution and 4 mg of Ni carrier were then added. The pH of the solutions was adjusted to 9 with concentrated NH_4OH. 5 mL of DMG solution (1% in ethanol) was then added. The obtained solutions were heated at 50°C during 30 min so as to favour the precipitation of the $Ni(DMG)_2$ complex. The precipitates were collected by filtration and washed with water. Thereafter, Ni was recovered by pouring gently 5 M HCl on the precipitate. Afterwards, the solutions were evaporated near to dryness (otherwise insoluble black residues were obtained as indicated in Ref. [26]). DMG was then decomposed with hydrogen peroxide. Thereafter, the obtained solutions were evaporated to dryness and the residues were dissolved in 10 mL of 0.5 M HCl. Finally, a 5 mL aliquot of the ^{63}Ni purified samples was prepared for LSC as described above.

Method 3 based on the precipitation of the $Ni(DMG)_2$ complex on Ni resin

Method 3 is based on the precipitation of the $Ni(DMG)_2$ complex on Ni resin [23]. It corresponds to the radiochemical method described by Eichrom Technologies [26] and applied in many reported works [6, 12, 13, 15, 17, 27]. Aliquots of the digested samples were first weighed in a beaker and 2 mg of Ni carrier were then added. After the addition of 5 mL concentrated HCl, the solutions were evaporated to dryness and the residues were dissolved in a few mL of 1 M HCl. 1 mL of 1 M ammonium citrate (that was preliminary adjusted to pH 8-9 with NH_4OH) was then added. Afterwards, the pH of the solutions was adjusted between 8 and 9 with NH_4OH. The samples were then loaded on the prepared Ni columns. The pre-packed Ni columns were preliminary conditioned with 20 mL of 0.2 M ammonium citrate that was adjusted to pH 8-9 with NH_4OH. After the loading of the samples, the Ni columns were rinsed with 20 mL of 0.2 M ammonium citrate (that was adjusted to pH 8-9 with NH_4OH) to eliminate the interfering elements. Thereafter, Ni was stripped with 5 mL of 3 M HNO_3. Finally, a 5 mL aliquot of the ^{63}Ni purified samples was prepared for LSC as described above. In those conditions, our group checked that the presence of 3 M HNO_3 and DMG did not induce any quenching effect in LSC by performing the protocol with a ^{63}Ni standard. Eichrom Technologies recommend to eliminate Fe prior to the separation on Ni column [26] but no threshold of

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

Results and discussion

Speciation studies

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

three ^{63}Ni radiochemical methods studied by our group. For that purpose, speciation calculations were made with JChess software (Ecole des Mines ParisTech, France). The database of the software (chess.tdb) was enriched with specific stability constants of Ni, Co and Fe with ammonia, citrate, tartrate and DMG (the stability constants related to hydroxide complexes and precipitates were already included). The relevant stability constants were obtained from Smith and Martell [28]. As citric acid has three acidic functions (the corresponding pKa values are: pKa1 = 3.1, pKa2 = 4.8, pKa3 = 6.4) [28], it was denoted as H_3Cit. In the same way, tartaric acid was denoted as H_2Tart (the corresponding pKa values are: pKa1 = 2.7, pKa2 = 3.7) [28]. Simple calculations were first performed by investigating the behaviours of Ni, Co and Fe in NaOH and NH_4OH. Whatever their quantities, Ni, Co and Fe are predicted to precipitate quantitatively with hydroxide ions by using NaOH. Fe is foreseen to precipitate and can also co-precipitate avec Co in NH_4OH medium, depending on their quantities. With regard to Ni, its predominant species are $Ni(NH_3)_x^{2+}$ complexes by using NH_4OH: no significant Ni precipitation is predicted at basic pH. Those results were in agreement with the experimental studies of Hou et al. [6], which proves the reliability of our JChess calculations.

The results obtained from JChess software are presented for the S2 steel sample (its chemical composition is given in Table 1) but similar conclusions can be drawn for the other materials, such as the S1 evaporate concentrate. The theoretical distribution diagrams of Ni(II), Co(II) and Fe(III) species are depicted respectively in Figures 1 to 3 for method 1. In the case of method 1, after the treatement of the sample in HNO_3, sodium citrate was added and pH was adjusted to 3-4 with NH_4OH. From JChess calculations, the predominant Ni(II) species are Ni^{2+}, $Ni(NO_3)^+$ and Ni-citrate complexes ($NiCit^-$ and NiH_2Cit^+) at pH 3-4. Those results are consistent with the work of Zelenin et al. who investigated the interaction of the Ni(II) ion with citric acid in an aqueous solution [35]. It is predicted that Co has the same behaviour as Ni at pH 3-4: the predominant Co(II) species are Co^{2+}, $Co(NO_3)^+$ and Co-citrate complexes ($CoCit^-$ and CoH_2Cit^+). In those pH conditions, the predominant Fe(III) species are Fe-citrate complexes (FeCit and $FeOHCit^-$). For method 1, no precipitation is predicted at pH 3-4. Consequently, after the addition of hydrogen peroxide, Co can be complexed by 2-

nitroso-1-naphthol and further extracted by chloroform [34], which induces an efficient elimination of Co. From literature [34], Fe can also be partly extracted. In this step, Ni which was not complexed by 2-nitroso-1-naphthol remained in the aqueous phase. The pH of the aqueous solution was then adjusted to 9 with ammonia. The speciation studies indicate that the predominant Ni(II) species are $Ni(NH_3)_x^{2+}$ complexes at pH 9, which prevents Ni from precipitating at basic pH. This is not the case for Fe which might start precipitating as Fe_2O_3 hematite when the pH is higher than 6. After the pH adjustment at 9, DMG was added. It can be noted that no stability constant was found for Fe with DMG: no stable complex might be formed [28]. On the contrary, the predominant Ni(II) species is the $Ni(DMG)_2$ complex at pH 9, which is in agreement with Dyrssen et al. [36]. Consequently, only Ni can be extracted in the organic phase after the addition of chloroform, which enables a selective purification of Ni for method 1. However, the presence of Fe precipitate might hinder the Ni extraction and induce a slight decrease of Ni recovery yield. Finally, Ni can be back-extracted at low pH in HCl medium for LSC analysis.

Concerning method 2, after the addition of tartaric acid and the pH adjustment with ammonia, the same Ni(II) species as above might be observed: the $Ni(NH_3)_x^{2+}$ complexes are predicted to be predominant at pH 8-9. In contrast, despite the use of tartaric acid, Co and Fe are foreseen to precipitate as $CoFe_2O_4$ and Fe_2O_3 at basic pH. The complexing properties of this chelating agent are not sufficient to prevent Co and Fe precipitation in the case of steels (the formation constant of Fe_2O_3 hematite is much greater than the one of $FeTart^+$ [28]). Afterwards, DMG was introduced in the aqueous solution. Since high amounts of Ni and DMG were used for method 2, the $Ni(DMG)_2$ precipitate is predicted to be formed. As Co and Fe are present as precipitates in the former step, a co-precipitation with $Ni(DMG)_2$ might occur. From speciation calculations, the main interfering elements, Co and Fe, are predicted to be not eliminated efficiently with method 2 in the case of a steel sample. Similar results were obtained for the other samples depending on Co and Fe quantities. It can be noticed that this point was not precisely specified in the French standard [21]. After the DMG precipitation step, the precipitate can be dissolved at low pH in concentrated HCl to recover Ni in solution.

The distribution diagrams of Ni(II), Co(II) and Fe(III) species related to method 3 are very close to those obtained for method 1 (see Figures 1 to 3). After the addition of ammonium citrate and the pH adjustment with ammonia, the predominant Ni(II) species are $Ni(NH_3)_x^{2+}$ complexes at pH 8-9. As the used quantity of citrate is quite low in method 3, at pH 8-9, Co and Fe exist as precipitate of $CoFe_2O_4$ and Fe_2O_3 in the case of steel sample. Similar conclusions were obtained for the other samples. Consequently, cautiousness has to be taken towards method 3 when Co or Fe are present in the analysed aliquots, which is in agreement with Eichrom Technologies' recommendations [26]. After the pH adjustment, the sample was loaded on the Ni resin which was preliminary conditioned with ammonium citrate at pH 8-9. Since high amounts of Ni and DMG are used for method 3, the $Ni(DMG)_2$ precipitate is predicted to be formed on the Ni column. After the rinsing step of the Ni column, concentrated HNO_3 was introduced. At pH lower than 1, the predominant Ni(II) species is predicted to be Ni^{2+} which allowed the Ni stripping from the column and its further LSC measurement.

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

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

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

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

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

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

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

$$E_n = \frac{\left| x_i - X_{method1} \right|}{\sqrt{\left(U_i^2 + U_{method1}^2 \right)}} \qquad \text{Eq. (1)}$$

Where

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

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

U_i is the expanded uncertainty of x_i

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

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

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

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

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

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

Conclusions

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

Acknowledgements

The authors thank the organizing committees of 17th RadChem and ERA12 conferences for allowing the oral presentations of this work.

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Table 1 Chemical and radiochemical compositions of studied nuclear waste samples

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

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

	Activity concentration (^{60}Co) (Bq g^{-1})	Activity concentration (^{63}Ni) (Bq g^{-1})			Ratio ^{63}Ni/^{60}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 x 10^2 ± 10%	2.76 x 10^2 ± 5%	2.50 x 10^2 ± 5%	2.88 x 10^2 ± 5%	0.3
Steel S2	1.10 x 10^4 ± 4%	3.99 x 10^3 ± 5%	3.37 x 10^3 ± 5%	3.82 x 10^3 ± 5%**	0.4
Muds embedded in concrete S3	1.38 x 10^4 ± 4%	8.94 x 10^3 ± 5%	n/a*	9.35 x 10^3 ± 5%	0.7
Effluent S4	2.10 ± 10%	1.39 ± 9%	1.18 x 10^1 ± 5%	1.45 ± 9%	0.7
Ion exchange resins S5	6.65 x 10^5 ± 4%	1.81 x 10^6 ± 4%	1.76 x 10^6 ± 4%	1.73 x 10^6 ± 4%	2.7
Graphite S6	4.05 x 10^3 ± 4%	2.78 x 10^4 ± 4%	n/a*	2.90 x 10^4 ± 4%	6.9
Ion exchange resins embedded in polymer S7	2.85 x 10^4 ± 4%	3.48 x 10^5 ± 4%	3.26 x 10^5 ± 4%	3.50 x 10^5 ± 4%	12.3
Ion exchange resins S8	4.67 x 10^3 ± 4%	7.66 x 10^4 ± 4%	6.57 x 10^4 ± 4%	7.95 x 10^4 ± 4%	16.4

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

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

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

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

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

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

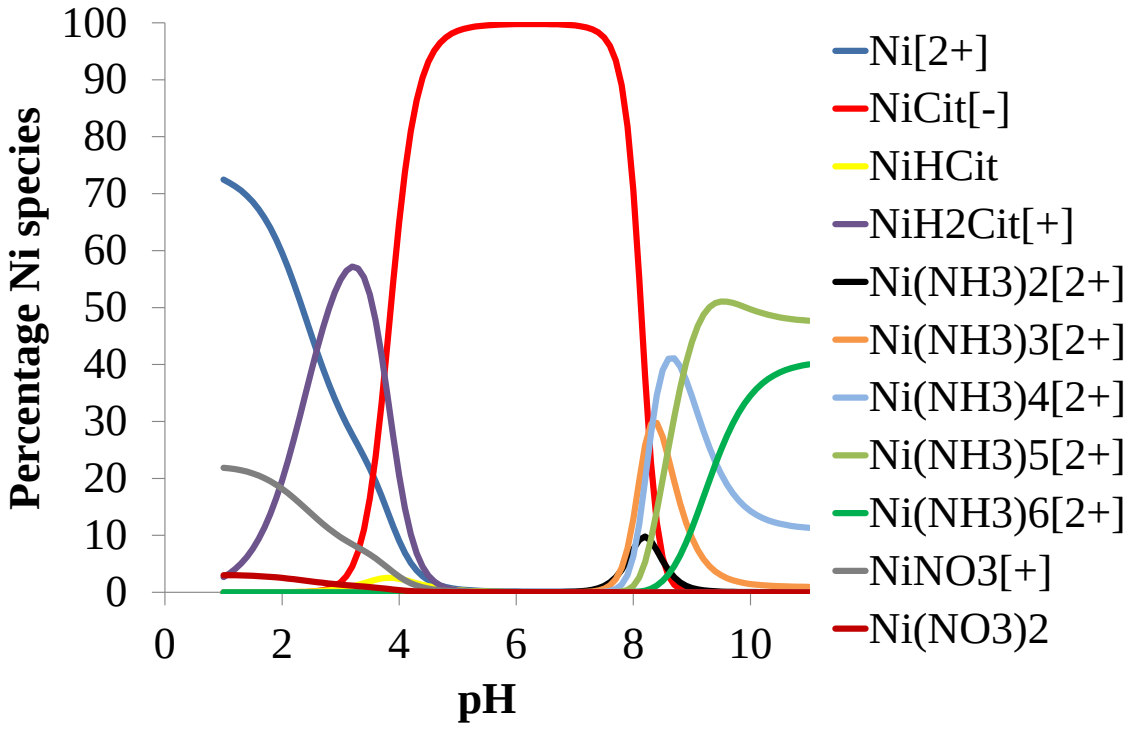

Fig. 2 Theoretical distribution diagram of Co(II) species for a steel (using JChess software)

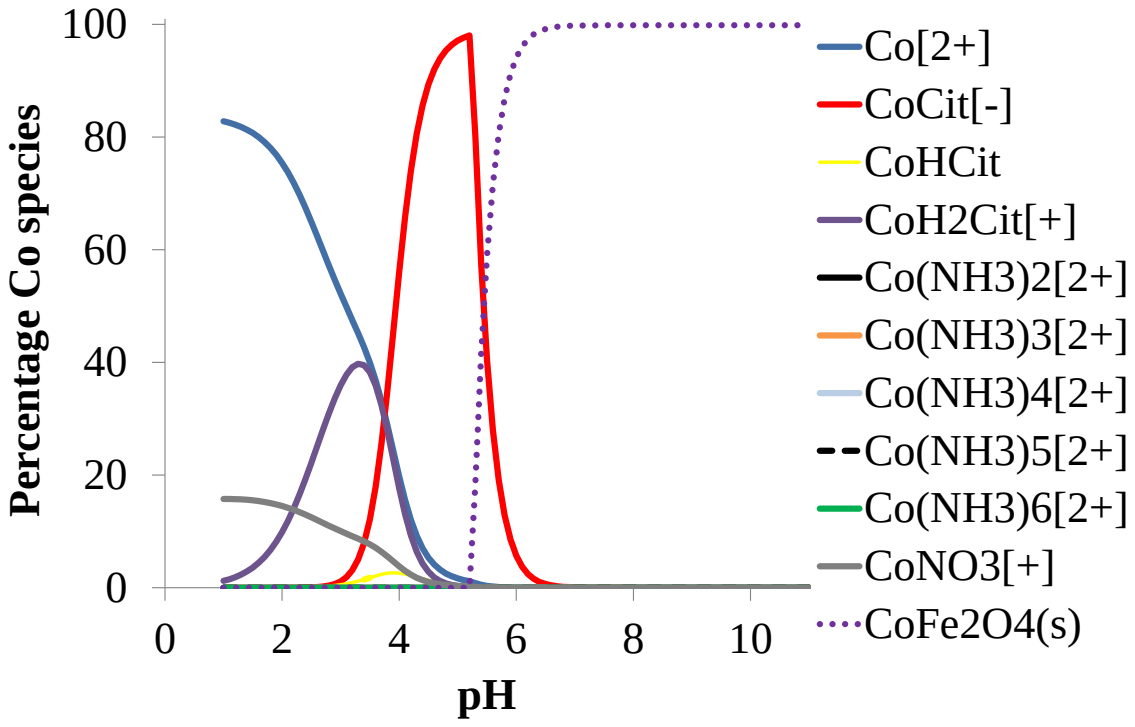

Fig. 3 Theoretical distribution diagram of Fe(III) species for a steel (using JChess software)

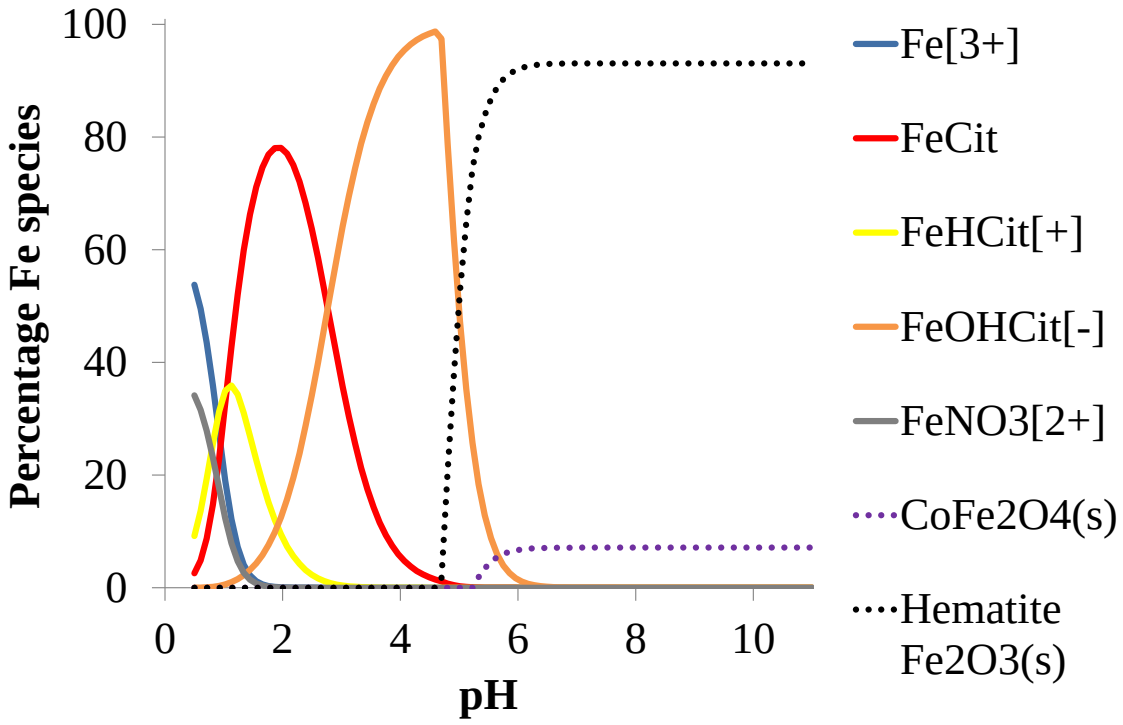

Fig. 4 Ni recovery yields (%) obtained for the three studied DMG-based radiochemical methods (n/a: not available)

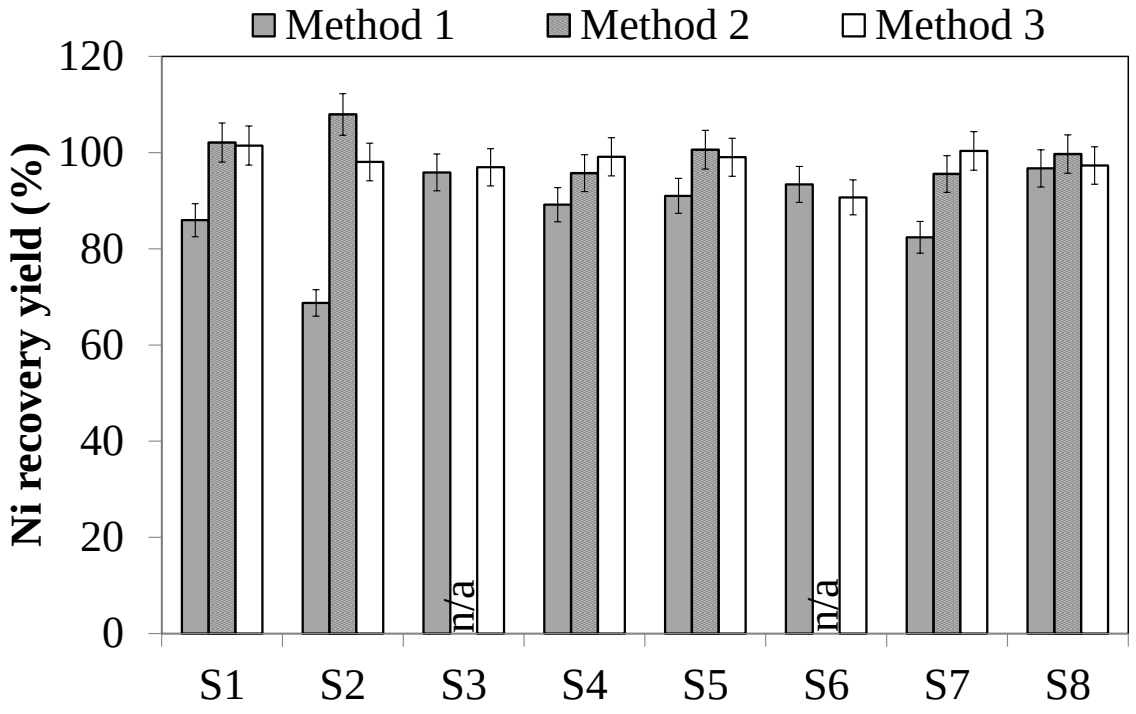
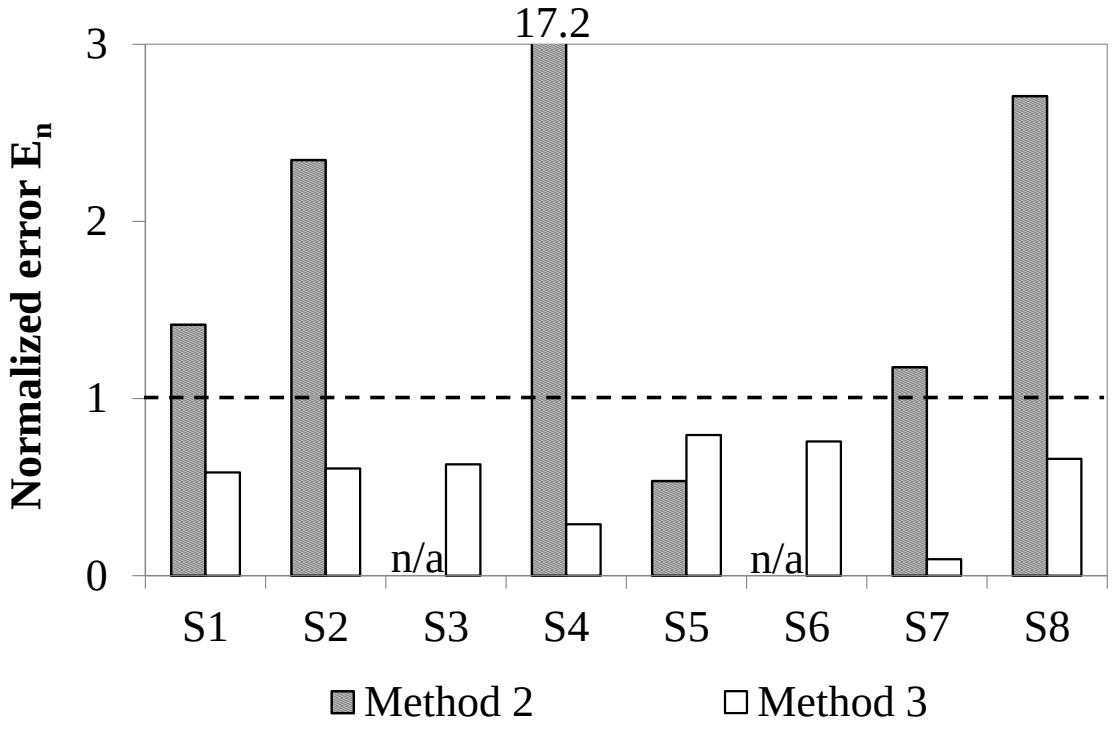
Fig. 5 Comparison of the studied DMG-based radiochemical methods in terms of normalized errors E_n (n/a: not available)