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Affinity of four different extraction chromatographic resin for Pd and Ag: Toward efficient separation of Pd from Ag

Leja Rovan Stiplošek [a,*], Mariella Van Ginkel [b], Michele Toma [b], Marko Štrok [a]

[a] Jožef Stefan Institute, Jamova cesta 39, SI-1000, Ljubljana, Slovenia
[b] Sapienza University of Rome, Piazzale Aldo Moro, 5, 00185, Roma, Italy

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ABSTRACT

In this study, the affinity of four extraction chromatographic resins from TrisKem International (TK200 Resin, Ni Resin, LN Resin, and TBP Resin) for retaining Pd and Ag in nitric and hydrochloric acid medium of various molarities was systematically investigated. Batch experiments were performed in which the resins were contacted with Pd and Ag solutions prepared in nitric and hydrochloric acids of different molarities. Affinity of specific resin for Pd and Ag was assessed with the help of distribution coefficients (K_d), defined as the ratio of the concentration of a specific element between resin and solution under equilibrium conditions, as a function of nitric and hydrochloric acid concentration. The results provided fundamental insight into behaviour of Pd and Ag in connection with different resin under varying chemical conditions and enabled design of optimum Pd and Ag column separation protocol. Among the resins investigated, Ni Resin and TK200 Resin exhibited the most favourable selectivity and separation performance, allowing efficient and reproducible Pd–Ag separation with high recoveries. For Ni Resin, the overall recovery was 92% for Pd and 98% for Ag, with a Pd separation factor of 2500±300. For TK200 Resin, the overall recovery was 89% for Pd and 98% for Ag, with a Pd separation factor of 770±80. However, an additional separation step would be required to achieve a higher separation factor when using TK200 Resin.

1. Introduction

The efficient separation of palladium (Pd) from silver (Ag) or vice versa is important for several applications, ranging from nuclear decommissioning and radioactive waste characterization to the production of radiopharmaceuticals. These elements often coexist in various matrices, including irradiated materials (Pd-109 and Ag-111), fission products (Pd-107 and Ag-107), and metallurgical or recycling samples such as spent catalysts and electronic waste, containing stable Pd and Ag [1–3].

In analytical chemistry, the co-existence of Pd and Ag in the sample can cause significant interferences in mass spectrometry due to ionization effects of matrix components or isobaric interferences created during the measurement. This issue is particularly relevant for Pd-107 analysis by Inductively Coupled Plasma Mass Spectrometry (ICP-MS), because stable Ag-107 produces a direct isobaric interference with Pd-107 [4]. Effective separation of Pd from Ag is necessary for accurate determination of isotopic compositions, to minimize matrix-induced ionization effects in mass spectrometry, and for the reduction of isobaric or spectral interferences that compromise measurement precision. In radiochemical analyses, chemical separation is crucial for isolating an analyte of interest from other interfering components present in a sample. Effective separation enables the detection of isotopes with low abundances or low-energy emissions, even in the presence of large quantities of other radioactive isotopes. This is particularly important in cases where there is an unavoidable presence of long-lived Ag-110m as a contaminant and where multi-step purification processes are required—such as extracting Ag-111 from the thorium matrix [5], or removing palladium target material from irradiated Ag-111 [1].

Separation of Pd from Ag remains challenging due to their similar chemical behaviour and overlapping physical properties, particularly the formation of stable chloride complexes [6–9]. Traditionally, this separation has relied on classical methods such as AgCl precipitation, solvent extraction, and ion-exchange chromatography [5,6,10–13]. While Ag precipitation is simple and highly selective, it is limited by co-precipitation and poor performance at trace levels. Solvent extraction and ion exchange offer improved selectivity but involve higher solvent consumption and operational complexity. In this context, extraction

* Corresponding author.
E-mail address: leja.rovan@ijs.si (L.R. Stiplošek).

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chromatography, where an extractant is adsorbed on a solid material, has emerged as a promising alternative, offering enhanced selectivity, faster separation kinetics, reduced solvent use, and lower acid waste generation, particularly for complex or dilute systems, and is increasingly recognized as an important approach for noble metal separation and preconcentration [14,15]. Previous studies on Pd/Ag separation using extraction chromatography have involved Ni Resin [4,7,16,17], as well as a two-step extraction chromatography procedure using LN Resin and TK200 Resin [1]. However, these studies report only specific conditions used for separation and do not an provide overall assessment of the affinity of these resins towards Pd and Ag over a range of nitric and hydrochloric acid concentrations. Therefore, a more extensive investigation of Pd-Ag separation was undertaken using four different extraction chromatography resins: TK200 Resin, Ni Resin, LN Resin, and TBP Resin.

TK200 Resin was selected because it is based on tri-n-octylphosphine oxide (TOPO), a widely used extractant in liquid–liquid extraction methods, particularly for actinide separation from acidic media [18]. TOPO has also been successfully applied for the extraction of various metal ions [19–21], and preliminary studies have indicated promising selectivity of TK200 Resin toward Pd and Ag [22].

Ni Resin contains dimethylglyoxime (DMG) as the extractant supported on an inert substrate and was selected for its high affinity toward transition metals and for its previous successful application in separating Pd [1,4,7,16]. The strong complexation with Pd (log K=34.1 at 25 °C) [23] suggests high selectivity for Pd(II) across a range of acid concentrations, making Ni Resin a strong candidate for achieving effective Pd separation.

LN Resin was chosen due to its well-established performance in the separation of lanthanides, actinides, and transition metals in nitric and hydrochloric acid media [24,25]. The resin is made up of the bis (2-ethylhexyl)phosphoric acid (HDEHP) compound, which provides strong affinity toward soft metal ions such as Pd(II), suggesting potential applicability for Pd–Ag separation under low acid concentrations conditions.

TBP (tri-n-butyl phosphate) is one of the classical extractants used in actinide and fission product separations, particularly in the PUREX process [26,27]. In the form of TBP Resin, it is comprised of an inert support impregnated with TBP, which allows it to be used in column extractive chromatographic separations. This resin served as a reference material to evaluate its potential for Pd and Ag separation given its known extraction behaviour in HCl media.

TK200 Resin, Ni Resin, LN Resin, and TBP Resin were selected to evaluate their effectiveness for Pd and Ag separation. While most other extraction chromatographic resins are optimized for actinides (UTEVA Resin, TEVA Resin, DGA Resin), these four resins cover complementary mechanisms—anion exchange (TK200 Resin), chelation (Ni Resin), cation exchange (LN Resin), and solvent extraction (TBP Resin)—suitable for noble metal recovery. This allowed the assessment of each resin's individual selectivity and efficiency under acidic conditions.

Understanding the distribution behaviour of Pd and Ag under varying chemical conditions is therefore essential for the rational design of separation strategies. Examination of the distribution coefficient (K_d) and related parameters enables prediction of optimal retention and elution conditions, thereby facilitating the development of a selective and efficient separation method for Pd and Ag.

The distribution coefficient (K_d) is a key parameter in the design of chromatographic separation methodologies, as it quantitatively describes the partitioning of an analyte between the resin and the aqueous phase under defined chemical conditions. By evaluating K_d values across different nitric and hydrochloric acid concentrations, insights can be gained into the affinity of specific resins for Pd and Ag, allowing the identification and optimization of conditions that promote effective retention and subsequent recovery of these elements from the resin [28].

The main objective of this study was to characterize the affinity of TK200 Resin, LN Resin, TBP Resin, and Ni Resin toward Pd and Ag to design an optimal column separation protocol. Batch experiments were conducted to evaluate the distribution of Pd and Ag between the investigated resins and varying concentrations of nitric and hydrochloric acid solutions. The results were evaluated in terms of distribution coefficients (K_d), which enabled the selection of the most promising conditions for separation of Pd from Ag. Based on this selection, column separation protocols were designed and tested with the aim of identifying the protocol with the best separation performance. Furthermore, as systematic distribution data for Ag and Pd on extraction chromatographic resins are currently scarce, this study provides a consistent K_d dataset to support the future development of rational Ag/Pd separation systems.

2. Materials and methods

2.1. Reagents and standards

TraceCERT® Pd and Ag single-element standards (1 g L^{-1}) were purchased from Sigma-Aldrich. Extraction chromatographic resins TK200 Resin, LN Resin, TBP Resin, and Ni Resin, each with a particle size of 100–150 μm, were obtained from TrisKem International.

All acids and reagents used were of analytical grade and obtained from commercial suppliers. Deionized water (≥18 MΩ·cm) was used throughout the experiments.

2.2. Determination of distribution coefficient (K_d)

The distribution of Pd and Ag between TK200 Resin, LN Resin, TBP Resin, and Ni Resin, and different concentrations of HNO_3 and HCl solutions, was determined by equilibrating a known volume of acid solution of selected concentration, spiked with a Pd and Ag mixed solution, with a known mass of resin. Approximately 0.3 g of each resin was weighed into 10 mL centrifuge tubes containing 20 μg of Pd and Ag in solutions of either HNO_3 or HCl at concentrations of 0, 0.01, 0.1, 1, 3, 6, 9 mol L^{-1}, as well as concentrated HCl (12.1 mol L^{-1}) or concentrated HNO_3 (14.4 mol L^{-1}), to a total volume of 10mL. The samples were shaken for 24 hours to ensure the establishment of equilibrium conditions. Equilibrium beyond this period was not investigated in detail, as longer equilibration times would not be practical for applications requiring relatively rapid Pd and Ag separation. After equilibration, the mixtures were filtered through 0.45 μm filters, and an aliquot of the aqueous phase was taken, diluted with 2 % HNO_3, and analysed by ICP-MS to determine the remaining analyte concentration in the aqueous phase. All experiments were performed in triplicate. The distribution coefficient was calculated according to the following equation [29]:

$$K_d = \left(\frac{c_{a,0} - c_a}{c_a}\right).\frac{m}{m_R} \quad (1)$$

where $c_{a,0}$ is the aqueous phase concentration of either Pd or Ag before contacting the solution with the resin [ng g^{-1}], c_a is the aqueous phase concentration of either Pd or Ag after contacting the solution with the resin [ng g^{-1}], m is the mass of the solution [g] and m_R is the mass of the resin [g].

Measurement uncertainties were calculated according to EURACHEM-CITAC recommendations [30] and are reported as combined standard uncertainties with a coverage factor of 2. All results are reported as a mean values of three replicates and accompanied with the combined standard uncertainties.

2.3. Development of optimum column separation protocol

The column separation protocol was developed based on the results of K_d values for Pd and Ag, and the most promising separation conditions identified from these data were subsequently tested in column experiments.

During the initial testing of the Pd–Ag separation process, the influence of column geometry (diameter and shape) and resin mass was assessed. Based on these studies, gravity-flow columns with an internal diameter of 7 mm, packed with approximately 0.3 g of resin (corresponding to a bed height of ~3 cm), were selected for all subsequent separations. The columns were operated under gravity flow with an approximate flow rate of 1 mL min^{-1}.

For Ni Resin, a standard solution containing 20 µg each of Pd and Ag each was prepared in 10 mL of 0.5 M HCl. The resin was preconditioned with 10 mL of 0.5 M HCl prior to sample loading. The sample was then loaded onto the column under gravity flow. Ag was eluted using three successive 10 mL aliquots of 0.5 M HCl, with each fraction collected separately. Subsequently, Pd was eluted using three 10 mL aliquots of 3 M HNO_3, and the fractions were collected individually.

For TK200 Resin, a standard solution containing 20 µg each of Pd and Ag was prepared in 10 mL of 0.1 M HNO_3 The column (packed with ~0.3 g of resin) was preconditioned with 0.1 M HNO_3 prior to sample loading. Under these conditions, Ag was eluted first using three 10 mL aliquots of 0.1 M HNO_3. Subsequently, Pd was eluted using three 10 mL aliquots of 6 M HNO_3, with all fractions collected separately.

The LN Resin was also evaluated for potential Pd and Ag separation, based on its favourable distribution coefficients and previous reports of successful applications in similar systems [1]. In the modified procedure, the resin was preconditioned with 10 mL of 0.1 M HNO_3. The sample solution (prepared in 0.1 M HNO_3) was loaded onto the column, after which Pd was first eluted using three 10 mL aliquots of 0.1 M HNO_3. Ag was subsequently eluted using three 10 mL aliquots of 1 M HCl, with fractions collected separately.

Aliquots of all collected fractions were diluted in 2 % HNO_3 and analysed by ICP-MS to determine the concentrations of Pd and Ag in each fraction and assess the separation efficiency.

For each resin showing effective separation, the separation factor ($SF_{Pd/Ag}$) was calculated to quantify the degree of Pd separation relative to Ag. The separation factor was defined as:

$$SF_{Pd/Ag} = \frac{(C_{Pd}/C_{Ag})after}{(C_{Pd}/C_{Ag})before} \quad (2)$$

where C_{Pd} and C_{Ag} are the concentrations of Pd and Ag, respectively, measured after separation (in the collected fractions) and before separation (in the initial solution).

Uncertainties were evaluated following EURACHEM-CITAC [30] and reported as combined expanded uncertainties (coverage factor k = 2).

2.4. Measurements

The analyte concentrations were measured using a triple-quadrupole inductively coupled plasma mass spectrometer (ICP-QQQ-MS), the Agilent 8800 (Agilent Technologies, Japan). The analytes of interest were measured in non-gas mode without mass shift. The instrument was equipped with a micro-mist nebuliser, a Scott-type spray chamber, and an ASX-510 (Cetac) autosampler. The exact concentrations of each analyte were determined using a calibration curve with single-element standards ranging from 0 to 100 ng g^{-1}. All samples were appropriately diluted in a mixture of 2 % HNO_3 and HCl prior to analysis. Additionally, rinse solutions containing a maximum of 5 % HNO_3 and HCl were used to prevent Pd from adhering to the components of the sample introduction system in contact with the sample solutions.

3. Results and discussion

3.1. Affinity of extraction resin for Pd and Ag

The affinity of selected extraction resins for Pd and Ag was evaluated in terms of the retention of Pd and Ag on different resins under various concentrations of HNO_3 and HCl solutions. This was expressed as the distribution coefficient (K_d) between the resin and the acid solution at specific molarity and for a given element. A high K_d value indicates that the resin has a strong affinity for the analyte, whereas a low K_d value indicates that the analyte does not interact significantly with the resin and remains predominantly in the acidic solution.

3.1.1. TK200 resin

The K_d data for Pd and Ag on the TK200 Resin in both HNO_3 and HCl media are shown in Fig. 1. For Pd in HNO_3 solutions (Fig. 1A), high retention on the resin is observed at lower acid concentrations (up to 1 M HNO_3), with K_d values in the range of 10^4–10^5. At these lower acidities, Pd is expected to exist primarily as the hydrated aqua-ion $[Pd(H_2O)_4]^{2+}$, which is thought to readily interact with the TOPO functional groups of the resin via a solvating mechanism [31]. Above 1 M HNO_3, the K_d values decrease significantly ($<10^3$), indicating reduced retention. This trend is likely associated with the increasing formation of Pd–nitrate species (e.g., $[Pd(NO_3)_2(H_2O)_2]$), and the potential competition for resin sites by the extraction of HNO_3 itself, both of which would reduce the availability of the metal for extraction. In contrast, Ag exhibits relatively low K_d values across the entire range of HNO_3 concentrations, suggesting weak interactions with the TK200 Resin. This behaviour may reflect the high stability of Ag^+ in the aqueous phase and a limited affinity of the silver ion for the TOPO extractant under these conditions. In HCl solutions (Fig. 1B), Pd again shows strong retention at lower concentrations (between 0.01 M and 0.1 M). As HCl concentrations increases above 1 M, K_d values decrease markedly. This observation aligns with established speciation models which indicate that a higher chloride activities, Pd(II) is converted into anionic chloro-complexes, primarily $[PdCl_4]^{2-}$ [32]. Because TOPO typically functions as a neutral solvating extractant, the formation of these stable anionic species likely hinders the extraction process, leading to the observed drop in K_d. Ag displays consistently lower K_d values throughout the entire HCl concentration range, suggesting very weak interaction with the resin under chloride conditions as well.

The largest difference in K_d values between Ag and Pd, which could be potentially used for separation of both elements, is observed in the 0.1–1 M HNO_3 concentration range. Under these conditions, TK200 Resin more strongly retains Pd compared to Ag.

3.1.2. Ni resin

The K_d values for Pd and Ag on the Ni Resin are shown in Fig. 2. At low HNO_3 concentrations (<0.1 M) in Fig. 2A, Ag exhibits high retention with K_d values in the range of 10^4–10^5, while Pd shows moderate retention with K_d values around 10^3. In these dilute acid solutions, it is proposed that both Pd and Ag can form stable complexes with the DMG functional groups of the resin. This is consistent with the known ability of DMG to act as a selective chelating agent for late transition metals, forming stable square-planar complexes with Pd^{2+} [33]. As the HNO_3 concentration increases, both analytes gradually lose their affinity for the Ni Resin. Above 0.1 M HNO_3, the sharp decrease in K_d values suggests a destabilization of the metal-DMG interaction. This trend may be attributed to the protonation of the oxime groups on the DMG molecule; as the acidity increases, H^+ ions compete with the metal ions for the nitrogen and oxygen donor sites on the ligand, effectively inhibiting chelation [34]. In HCl media (Fig. 2B), Pd displays consistently high retention across the entire concentration range (K_d >10^3). This observation suggests that the Pd-DMG chelate remains thermodynamically stable even at higher chloride activities, where Pd might otherwise favour anionic chloro-species. In contrast, Ag shows negligible retention, except at very low HCl concentrations (0.001 M), where K_d values reach approximately 10^4. This behaviour likely reflects the rapid formation of silver-chloro complexes or the precipitation of AgCl within the resin matrix [35], both of which would reduce the concentration of free Ag^+ available for interaction with the resin's functional groups.

The largest potential for effective chemical separation between Pd and Ag is therefore in HCl media, particularly within the 0.1–6 M HCl

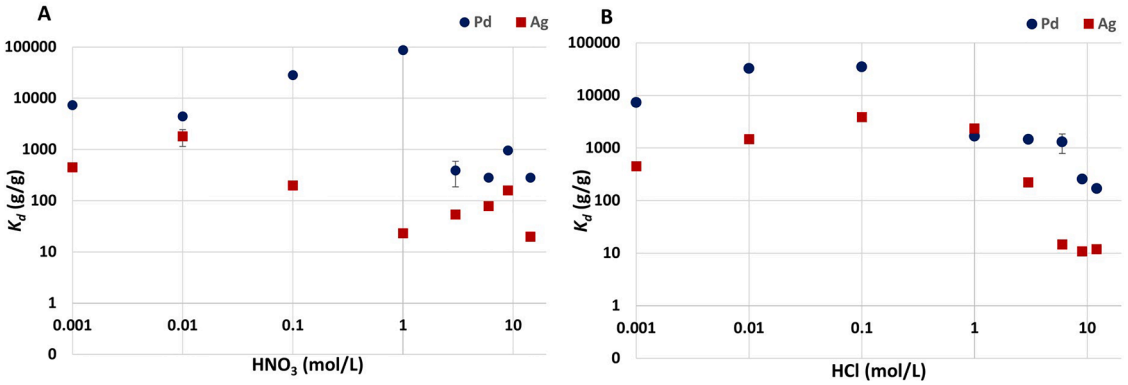

Fig. 1. Distribution coefficient (K_d) of Pd (blue circle) and Ag (red square) with expanded combined uncertainties (k=2) between TK200 Resin and HNO_3 (A) and HCl (B) solutions at selected concentrations. Where error bars are not visible, they are smaller than data points.

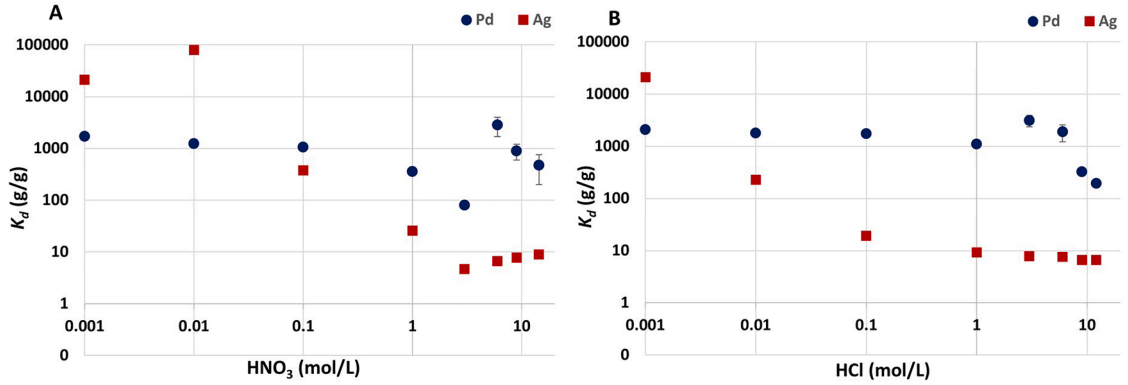

Fig. 2. Distribution coefficient (K_d) of Pd (blue circle) and Ag (red square) with expanded combined uncertainties (k=2) between Ni Resin and HNO_3 (A) and HCl (B) solutions at selected concentrations. Where error bars are not visible, they are smaller than data points.

concentration range. Under these conditions, Ni Resin has weak affinity for Ag and strong for Pd.

3.1.2. *LN resin*

In Fig. 3A, the affinity of LN Resin towards Pd and Ag in HNO_3 media is generally similar, with one notable difference at 0.1 M HNO_3. Under this condition, Pd shows significantly higher retention on the resin, with K_d values around 10^4, whereas Ag exhibits much lower retention, with K_d values around 10^2. This behaviour may be attributed to the different coordination preferences of the two metals; while Ag^+ in nitric media has a limited tendency to form stable chelates with organophosphorus extractants like HDEHP, Pd^{2+} is thought to interact more effectively with the phosphoryl oxygen and deprotonated hydroxyl groups of the extractant at low acidity [36]. In HCl media (Fig. 3B), Ag shows minor retention only at very low acid concentrations, while Pd displays consistently higher retention across the entire concentration range. The K_d values for Ag vary from approximately 10^3 at concentrations below 0.1 M to about 10^1 at higher concentrations. This trend likely reflects the shifting stability of silver-chloro species. At HCl concentrations below 0.1 M, Ag(I) is expected to exist as a mixture of cationic Ag^+ and neutral [AgCl] species, which may facilitate interaction with the HDEHP groups. At higher concentrations, the dominance of the monoanionic chloro-complex $[AgCl_2]^-$ is consistent with the observed decrease in retention, as anionic species typically exhibit minimal affinity for acidic

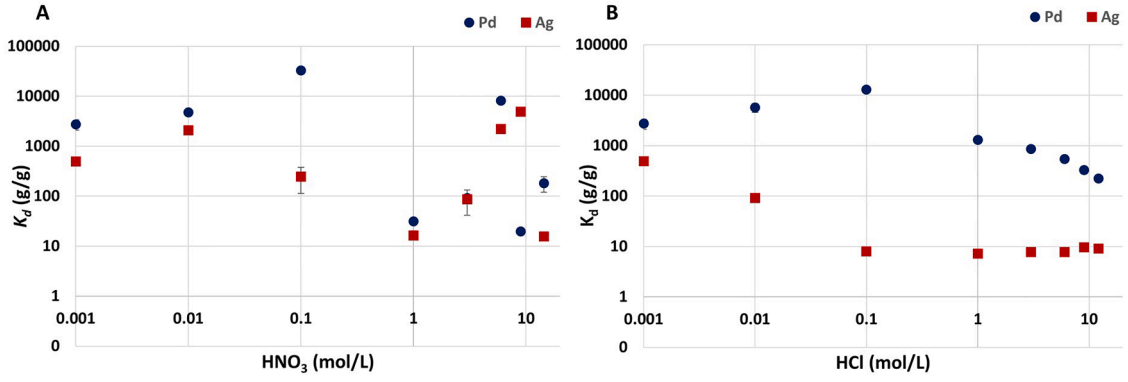

Fig. 3. Distribution coefficient (K_d) of Pd (blue circle) and Ag (red square) with expanded combined uncertainties (k=2) between LN Resin and HNO_3 (A) and HCl (B) solutions at selected concentrations. Where error bars are not visible, they are smaller than data points.

cation exchangers like HDEHP [37]. In contrast, K_d values for Pd remain in the range of 10^3–10^4 throughout all HCl concentrations. This consistent retention suggest that Pd may form various chloro-complex species capable maintaining an interaction with the HDEHP functional groups, possibly through a solvating mechanism or the formation of mixed-ligand complexes (Pd-Cl-HDEHP), as has been proposed for similar platinum group metal extractions in acidic chloride media [38].

The potential for effective separation of Pd and Ag using LN Resin is therefore the largest in HCl media, particularly within the 0.01–1 M HCl range, where the affinity of LN Resin for Pd remains large and for Ag remains small. Another potential separation window may also be in 0.1 M HNO_3, where Pd affinity on the LN Resin is large, while Ag affinity is small.

3.1.3. TBP resin

For both Pd and Ag, the K_d values for TBP Resin in HCl media range from 10^1 to 10^3, with higher retention observed at low HCl concentrations and negligible retention at higher concentrations (Fig. 4B). In HNO_3 media (Fig. 4A), K_d values showed no significant difference or measurable retention for either Pd or Ag. These results suggest that under the conditions evaluated, the formation of extractable neutral complexes between the analytes and the TBP functional groups is limited. In nitric acid, the high stability of the palladium aqua-ion and the specific solvation requirements of $Pd(NO_3)_2$ may account for the lack of retention; TBP is a neutral solvating extractant that generally requires high nitrate activities or high acid concentrations to effectively partition late transition metals [39]. Similarly, in HCl media, the decrease in retention at higher acidities is potentially consistent with the shift toward anionic chloro-complexes such as $[PdCl_4]^{2}$ and $[AgCl_2]^{-}$. As TBP primarily extracts neutral species through a solvation mechanism, it possesses a low affinity for these highly charged anions [40]. Thus, the TBP Resin appears to offer limited utility for the effective recovery of Pd or Ag under the specific mineral acid concentrations evaluated in this study.

Overall, the TBP resin showed no significant difference between the K_d values of Pd and Ag; therefore, no further testing was performed with this resin.

3.2. Pd and Ag separation experiments

When designing a chemical separation protocol of two elements using column extraction chromatography, it is important to select conditions in which the distribution coefficient (K_d) for one element remains high while that of the other remains low. This enables the retention of one element on the extraction resin on the column, while the other passes through the column. By subsequently modifying the elution conditions, the element initially retained on the stationary phase can be selectively eluted from the column. However, the exact K_d values are not always decisive in determining whether the separation using this method would be efficient, as they can be influenced by several factors, including resin batch variability, matrix effects, resin aging, etc. Therefore, for the purpose of designing an effective chemical separation protocol, the order of magnitude and general trends of the K_d values are more important than their precise numerical values.

Based on the K_d findings, further investigations were conducted to establish the most effective separation procedure for Pd and Ag. Among the investigated resins, TK200 Resin, Ni Resin, and LN Resin demonstrated promising separation potential, while TBP Resin showed negligible differentiation in retention between the two elements. Accordingly, the most promising conditions identified from the K_d studies were tested in column separation experiments.

For the TK200 Resin, 0.1 M HNO_3 was used for Ag elution and 6 M HNO_3 for Pd elution. For the Ni Resin, Ag was eluted first using 0.5 M HCl, followed by Pd elution with 3 M HNO_3. Additionally, the LN Resin was also tested, where Pd was stripped down with 0.1 M HNO_3 and then Ag with 1 M HCl. The aim was to further evaluate whether Pd and Ag could be effectively separated using this resin under optimized conditions.

3.2.1. Pd and Ag separation

The results of the separation of Pd from Ag or Ag from Pd are presented in Fig. 5. For the TK200 Resin (Fig. 5a), Ag was efficiently eluted in the first two 10 mL fractions using 0.1 M HNO_3, demonstrating the resin's low affinity for Ag under the selected conditions. Pd was subsequently eluted with three 10 mL 6 M HNO_3 fractions, indicating that higher HNO_3 concentrations effectively disrupt Pd–TOPO interactions and allow quantitative recovery. The overall recovery of Ag from TK200 Resin was 98 %, while Pd recovery reached 89 %, with approximately 3 % of Pd remaining adsorbed on the resin, likely due to incomplete elution or residual complexation. Measurement of Pd in the solution before and after column separation showed that a separation factor of approximately 770±80 ($SF_{Pd/Ag}$) was achieved through this process. While this value indicates effective separation, additional separation steps would be required to obtain a higher $SF_{Pd/Ag}$ and further improve purification.

A comparable separation performance was obtained with the Ni Resin (Fig. 5b). Ag was quantitatively eluted (98 %) in the first two fractions using 0.5 M HCl, highlighting the resin's low affinity for Ag under chloride conditions. Pd was then eluted with 3 M HNO_3 with three 10 mL fractions, achieving a total recovery of 92 %, while roughly 3 % of Pd remained bound to the column. These results indicate that Ni Resin provides a robust separation option, particularly when sequential elution with HCl and HNO_3 is employed, allowing efficient discrimination between Ag and Pd based on their differing chemical affinities. The separation factor ($SF_{Pd/Ag}$) between Pd and Ag, determined from measurements conducted before and after column separation, was

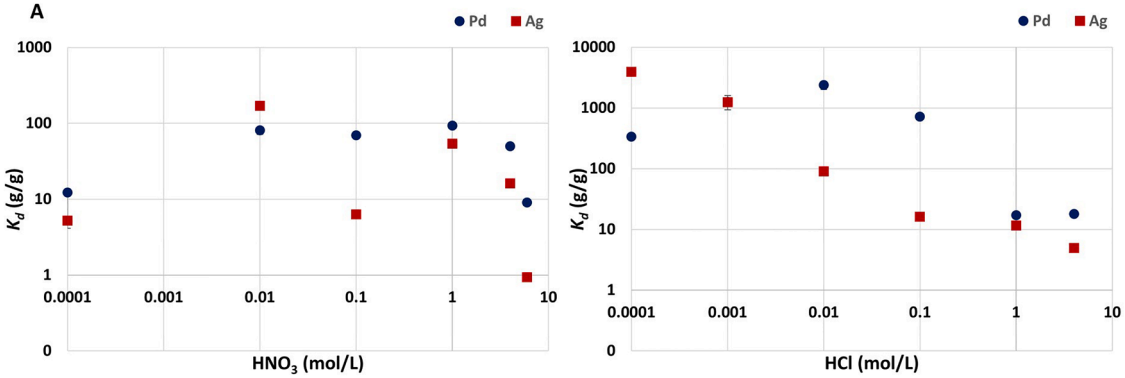

Fig. 4. Distribution coefficient (K_d) of Pd (blue circle) and Ag (red square) with expanded combined uncertainties (k=2) between TBP Resin and HNO_3 (A) and HCl (B) solutions at selected concentrations. Where error bars are not visible, they are smaller than data points.

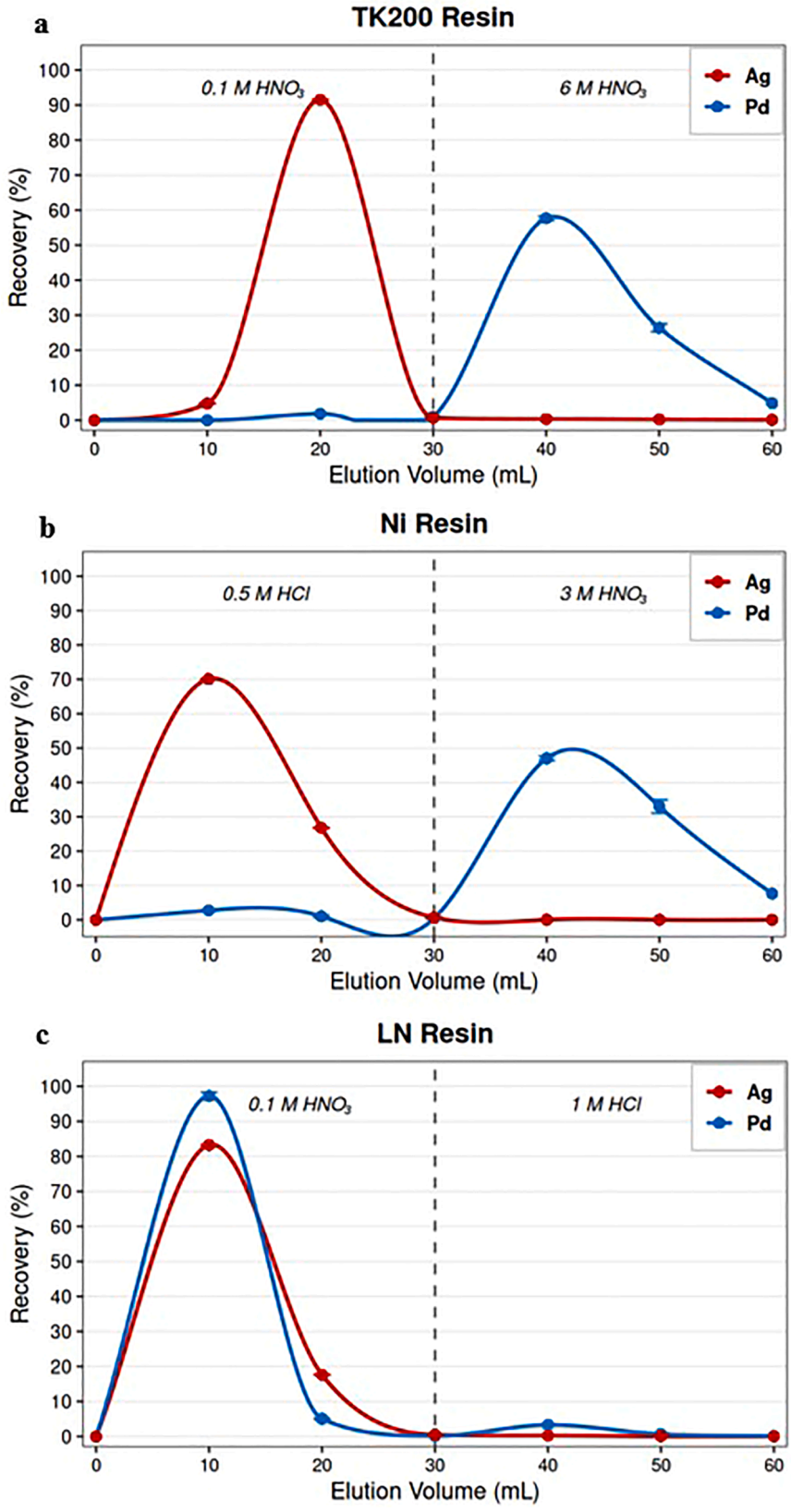

Fig. 5. Elution profiles of Pd (blue) and Ag (red) on TK Resin (A), Ni Resin (B) and LN Resin (C), with selected elution conditions and volumes and recoveries of each individual analyte. Uncertainty represents expanded combined uncertainties with coverage factor k=2 (where error bars are not visible, they are smaller than data points).

approximately 2500±300. This high separation factor demonstrates the strong selectivity of the resin for Pd over Ag and confirms its suitability for efficient and reliable Pd–Ag separation under the applied experimental conditions.

In contrast, the LN Resin demonstrated limited separation capability under the tested conditions (Fig. 5c). Both Ag and Pd were co-eluted in 0.1 M HNO_3, yielding 99 % Ag recovery and 96 % Pd recovery in the first two fractions. A small additional fraction of Pd was released with 1 M HCl, resulting in a total Pd recovery of 99 %. The partial co-elution suggests that LN Resin has insufficient selectivity between Pd and Ag under these conditions, likely due to similar complexation behaviour with the HDEHP functional groups in dilute acid. An additional experiment was conducted in which Pd was loaded onto the resin using 0.1 M HCl and subsequently eluted with 1 M HCl. However, the results showed that both Pd and Ag were again co-eluted with 0.1 M HCl.

Overall, these findings demonstrate that both TK200 Resin and Ni Resin enable effective and reproducible chemical separation of Pd and Ag, particularly when the tested Pd and Ag masses do not exceed 1 mg. Among the two, Ni Resin shows slightly higher Pd recovery and a cleaner elution profile. The results also highlight the importance of carefully optimizing acid concentration and sequential elution steps to maximize recovery and selectivity. In contrast, LN Resin is less suitable for practical Pd–Ag separation due to its limited discrimination between the two elements.

3.3. Possible applications of developed separation methods

3.3.1. Separation of Ag-111 from Pd target material for potential radionuclide therapy

Ag-111 ($t_{1/2} = 7.47$ d, $\beta_{max} = 1.04$ MeV) is a β^--emitting radionuclide that has been investigated for potential use in targeted radiotherapy. Its decay is accompanied by low-energy γ-emissions, primarily at 245 keV (1.24%) and 342 keV (6.7%), which may enable imaging using single-photon emission computed tomography (SPECT). This combination of β^- emission and γ radiation has led to consideration of Ag-111 as a candidate theranostic isotope, with the potential for concurrent therapeutic application and imaging-based monitoring, pending further validation in relevant systems [41]. Separation of Ag-111 from irradiated palladium targets is essential to obtain a chemically and radiochemically suitable product for subsequent studies. Residual Pd may interfere with radiolabeling processes and could affect the reproducibility of downstream applications. Efficient isolation of Ag-111 therefore important for achieving high radiochemical purity and for enabling reliable evaluation of its properties in future investigations [42].

Based on the results of this study, the Ni Resin appears to be a promising option for Ag/Pd separation under the tested conditions. It enables rapid separation, with Ag-111 eluted first in two fractions with an overall recovery of approximately 98 %, followed by Pd-109 in three fractions. The use of moderate acid concentrations (Ag-111 is eluted using 0.5 M HCl) may be advantageous for subsequent processing steps and could reduce handling challenges associated with highly concentrated acidic or radioactive waste streams. Further work is required to assess the applicability of this method under more realistic conditions. In particular studies involving irradiated Pd targets and larger target masses are needed to evaluate scalability and robustness. Validation using representative sample matrices is currently in progress, and comprehensive results will be presented in a subsequent study.

3.2.2. Determination of Pd-107 in radioactive waste

The determination of Pd-107 in radioactive waste is important for assessing long-term radiological behaviour and informing nuclear waste management strategies. Pd-107 is a long-lived radionuclide, with a half-life of approximately 6.5 million years, and may contribute to the long-time radioactivity of waste repositories [43]. Accurate quantification is therefore relevant for waste classification, storage planning, and regulatory compliance, minimizing potential environmental and health risks.

A key analytical challenge is the presence of chemical and isotopic interferences. Silver isotopes, particularly Ag-107, present a significant isobaric interference, sharing the same nominal mass as Pd-107 and potentially affecting radiochemical and mass-spectrometric measurements. In addition, complex waste matrices may influence Pd detection through signal suppression or enhancement [4]. Rigorous chemical purification is therefore required to separate Pd-107 from silver and other interfering species, reduce matrix effects, and enable reliable quantification with improved detection limits.

Based on the results of this study, Ni Resin appears to be a promising option for the effective separation of Pd-107 from isobaric interference by Ag-107 under the investigated conditions. The data indicate that Ag, and its isotope Ag-107, which is the primary source of isobaric and polyatomic interferences in mass spectrometric measurements, are efficiently eluted first using 0.5 M HCl. Subsequent elution with 3 M HNO_3 allows Pd to be stripped from the resin over three fractions, achieving an overall Pd recovery of 92 %. An alternative separation strategy for obtaining interference-free Pd-107 could involve the use of TK200 Resin. In this approach, Ag isotopes are first removed from the resin using 0.1 M HNO_3, followed by Pd elution with 6 M HNO_3, resulting in an overall Pd recovery of 89 %. While Ni Resin has been previously applied for Pd purification in radioactive waste analysis [4,7,16,17], the use of TK200 Resin represents an additional approach that may be suitable for reducing interferences prior to mass spectrometric analysis. Further work is needed to evaluate the performance of these separation methods in representative radioactive waste matrices. Studies involving real samples are currently in progress to assess robustness, potential matrix effects, and overall applicability under practical conditions.

4. Conclusion

This study established a comprehensive K_d dataset for Ag and Pd on TK200 Resin, Ni Resin, LN Resin, and TBP Resin, filling a significant gap in the literature and enabling the rational design of separation protocols. Systematic batch experiments revealed distinct differences in resin affinities, which were successfully translated into optimized column procedures.

Our evaluation identified Ni Resin and TK200 Resin as the most effective materials. Ni Resin demonstrated superior selectivity and robustness in hydrochloric acid media, providing the cleanest elution profiles and the highest recoveries. TK200 Resin emerged as a highly capable alternative, particularly for nitric acid-based systems. In contrast, TBP Resin and LN Resin were limited by poor selectivity or narrow operational windows, making them less suitable for high-purity separations.

The reliability of these methods suggests broad applicability in radiochemical workflows, most notably in the production of Ag-111 for medical therapy and the monitoring of Pd-107 in nuclear waste. Future work will focus on testing these optimized protocols with irradiated targets and complex sample matrices to confirm their performance under realistic conditions. Ultimately, this work highlights the necessity of systematic resin characterization and establishes a robust framework for efficient Ag/Pd separation in both analytical and radiochemical applications.

CRediT authorship contribution statement

Leja Rovan Stiplošek: Writing – original draft, Visualization, Validation, Supervision, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Mariella Van Ginkel:** Investigation. **Michele Toma:** Investigation. **Marko Štrok:** Writing – review & editing, Visualization, Validation, Supervision, Resources, Project administration, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

References

[1] M. Tosato, A. Gandini, S. Happel, M. Bas, A. Donzella, A. Zenoni, A. Salvini, A. Andrighetto, V. Di Marco, M. Asti, Chromatographic separation of silver-111 from neutron-irradiated palladium target: toward direct labeling of radiotracers, EJNMMI Radiopharm. Chem. 8 (2023) 43, https://doi.org/10.1186/s41181-023-00232-0.

[2] F.B. Biswas, I.M.M. Rahman, K. Nakakubo, K. Yunoshita, M. Endo, K. Nagai, A. S. Mashio, T. Taniguchi, T. Nishimura, K. Maeda, H. Hasegawa, Selective recovery of silver and palladium from acidic waste solutions using dithiocarbamate-functionalized cellulose, Chem. Eng. J. 407 (2021) 127225, https://doi.org/10.1016/j.cej.2020.127225.

[3] A.M. Safiulina, N.E. Borisova, E.A. Karpyuk, A.V. Ivanov, D.A. Lopatin, Extraction of palladium from spent nuclear fuel reprocessing solutions, Metals (Basel) 14 (2024) 133, https://doi.org/10.3390/met14020133.

[4] M. Faure, C. Gautier, P. Fichet, A. Maubert, E. Debonnet, E. Laporte, C. Colin, L. Hélot, Methods of separation and quantification by ICP-MS for Pd-107 in radioactive waste, J. Radioanal. Nucl. Chem. 334 (2025) 4687–4707, https://doi.org/10.1007/s10967-025-10147-6.

[5] T. Mastren, V. Radchenko, J.W. Engle, J.W. Weidner, A. Owens, L.E. Wyant, R. Copping, M. Brugh, F.M. Nortier, E.R. Birnbaum, K.D. John, M.E. Fassbender, Chromatographic separation of the theranostic radionuclide 111Ag from a proton irradiated thorium matrix, Anal. Chim. Acta 998 (2018) 75–82, https://doi.org/10.1016/j.aca.2017.10.020.

[6] S.T. Lancaster, B. Russell, T. Prohaska, J. Irrgeher, Isobaric interference removal for selected radionuclides using nitrous oxide and ammonia with inductively coupled plasma tandem mass spectrometry, J. Anal. At. Spectrom. 40 (2025) 3210–3220, https://doi.org/10.1039/D5JA00254K.

[7] A. Weller, T. Ramaker, F. Stäger, T. Blenke, M. Raiwa, I. Chyzhevskyi, S. Kirieiev, S. Dubchak, G. Steinhauser, Detection of the fission product palladium-107 in a pond sediment sample from chernobyl, Environ. Sci. Technol. Lett. 8 (2021) 656–661, https://doi.org/10.1021/acs.estlett.1c00420.

[8] T.M. Seward, The stability of chloride complexes of Silver in hydrothermal solutions up to 350°C, Geochim. Cosmochim. Acta 40 (1976) 1329–1341, https://doi.org/10.1016/0016-7037(76)90122-8.

[9] J.-F. Boily, T.M. Seward, Palladium(II) chloride complexation: Spectrophotometric investigation in aqueous solutions from 5 to 125°C and theoretical insight into Pd-Cl and Pd-OH2 interactions, Geochim. Cosmochim. Acta 69 (2005) 3773–3789, https://doi.org/10.1016/j.gca.2005.03.015.

[10] C. Blackadar, K.-Y.G. Choi, M.F. Embree, H.M. Hennkens, C. Rodríguez-Rodríguez, R.E.W. Hancock, K. Saatchi, U.O. Häfeli, SPECT/CT Imaging of 111 Ag for the preclinical evaluation of silver-based antimicrobial nanomedicines, ACS Appl. Mater. Interfaces 14 (2022) 26382–26393, https://doi.org/10.1021/acsami.2c03609.

[11] R. Alberto, P. Bläuenstein, I. Novak-Hofer, A. Smith, P.A. Schubiger, An improved method for the separation of 111Ag from irradiated natural palladium, Int. J. Rad. Appl. Instrum. A 43 (1992) 869–872, https://doi.org/10.1016/0883-2889(92)90148-8.

[12] K. Aardaneh, H.G. Raubenheimer, T.N. Van der Walt, C. Vermeulen, N. Van der Meulen, Separation of 103Pd from Rh and Ag by the macroporous AG MP-1 anion exchange resin in Ag targets, J. Radioanal. Nucl. Chem. 256 (2003) 31–35, https://doi.org/10.1023/A:1023387606697.

[13] S. Asai, T. Yomogida, M. Saeki, H. Ohba, Y. Hanzawa, T. Horita, Y. Kitatsuji, Determination of ^{107} pd in pd recovered by laser-induced photoreduction with inductively coupled plasma mass spectrometry, Anal. Chem. 88 (2016) 12227–12233, https://doi.org/10.1021/acs.analchem.6b03286.

[14] M. Rievaj, E. Culková, D. Šandorová, J. Durdiak, R. Bellová, P. Tomčík, A review of analytical techniques for the determination and separation of silver ions and its nanoparticles, Nanomaterials 13 (2023) 1262, https://doi.org/10.3390/nano13071262.

[15] A.M. Safiulina, N.E. Borisova, E.A. Karpyuk, A.V. Ivanov, D.A. Lopatin, Extraction of palladium from spent nuclear fuel reprocessing solutions, Metals (Basel) 14 (2024) 133, https://doi.org/10.3390/met14020133.

[16] S. Dulanská, B. Horváthová, B. Remenec, Ľ. Mátel, Determination of 107Pd in radwaste using Ni ®resin, J. Radioanal. Nucl. Chem. 310 (2016) 645–650, https://doi.org/10.1007/s10967-016-4827-0.

[17] M. Shmeit, M. Faure, C. Gautier, H. Isnard, Quantifying the accurate content of 107Pd in a radioactive effluent using the isotope dilution technique and multi-collector ICP-MS, Spectrochim. Acta Part B At. Spectrosc. 225 (2025) 107119, https://doi.org/10.1016/j.sab.2025.107119.

[18] Z. Wang, Z. Huang, Y. Xie, Z. Tan, Method for determination of Pu isotopes in soil and sediment samples by inductively coupled plasma mass spectrometry after simple chemical separation using TK200 resin, Anal. Chim. Acta 1090 (2019) 151–158, https://doi.org/10.1016/j.aca.2019.08.063.

[19] Tibor. Braun, G.. Ghersini, Extraction Chromotography, Elsevier, 1975.

[20] D. Choudhury, S. Lahiri, T. Nag, S. Sodaye, A. Bombard, Separation of bulk Pb and Bi from proton irradiated lead bismuth eutectic (LBE) target by DGA-N and TK-200 resins, J. Radioanal. Nucl. Chem. 324 (2020) 897–902, https://doi.org/10.1007/s10967-020-07113-9.

[21] T. SATO, K. SATO, Y. NOGUCHI, Liquid-liquid extraction of mercury (ii) from hydrochloric and nitric acid solutions by trioctyl phosphine oxide, Shigen-to-Sozai 117 (2001) 880–884, https://doi.org/10.2473/shigentosozai.117.880.

[22] TRISKEM INTERNATIONAL, PRODUCT SHEET TK200 Resin, 2017. Bruz France, www.triskem.com.

[23] A.E. Martell, R.M. Smith, in Oximes, Other Organic Ligands, Springer US, Boston, MA, 1977, pp. 306–309, https://doi.org/10.1007/978-1-4757-1568-2_13.

[24] F. Monroy-Guzman, C. del C. De la Cruz Barba, E. Jaime Salinas, V. Garibay-Feblés, T.N. Nava Entzana, Extraction chromatography materials prepared with HDEHP on different inorganic supports for the separation of gadolinium and terbium, Metals (Basel) 10 (2020) 1390, https://doi.org/10.3390/met10101390.

[25] W. Zhang, D. Feng, X. Xie, X. Tong, Y. Du, Y. Cao, Solvent extraction and separation of light rare earths from chloride media using HDEHP-P350 system, J. Rare Earths 40 (2022) 328–337, https://doi.org/10.1016/j.jre.2021.05.003.

[26] TRISKEM INTERNATIONAL, PRODUCT SHEET TBP resin, 2015. Bruz France, www.triskem.com.

[27] F.H. Ikhwan, H. Kazama, C. Abe, K. Konashi, T. Suzuki, Behaviors of actinides in chromatographic separation by using TBP resin in nitric acid solution and hydrochloric acid solution, J. Nucl. Sci. Technol. 61 (2024) 375–383, https://doi.org/10.1080/00223131.2023.2231937.

[28] M. Snow, J. Ward, Fundamental distribution coefficient data and separations using eichrom extraction chromatographic resins, J. Chromatogr. A 1620 (2020) 460833, https://doi.org/10.1016/j.chroma.2019.460833.

[29] H. Small, The chromatographic process, in: ion chromatography, Springer US, Boston, MA, 1989: pp. 11–39. https://doi.org/10.1007/978-1-4899-2542-8_2.

[30] S.L.R. Ellison, A. Williams, Eurachem/CITAC guide: Quantifying Uncertainty in Analytical Measurement, Third edition, 2012. www.eurachem.org.

[31] J. Purans, B. Fourest, C. Cannes, V. Sladkov, F. David, L. Venault, M. Lecomte, Structural investigation of pd(ii) in concentrated nitric and perchloric acid solutions by XAFS, J. Phys. Chem. B 109 (2005) 11074–11082, https://doi.org/10.1021/jp045489n.

[32] M. Wojnicki, R.P. Socha, Z. Pędzich, K. Mech, T. Tokarski, K. Fitzner, Palladium(ii) chloride complex ion recovery from aqueous solutions using adsorption on activated carbon, J. Chem. Eng. Data 63 (2018) 702–711, https://doi.org/10.1021/acs.jced.7b00885.

[33] I. Singh, P.S. Kadyan, B.S. Garg, S. Barua, 4-(2-Quinolylazo)phenol as a spectrophotometric reagent for palladium(ii), osmium(viii), and gold(III), Bull. Chem. Soc. Jpn. 62 (1989) 1316–1320, https://doi.org/10.1246/bcsj.62.1316.

[34] H. Hashemi-Moghaddam, A selective flotation-spectrophotometric method for the determination of nickel using dimethylglyoxime, J. Braz. Chem. Soc. 22 (2011) 1056–1060, https://doi.org/10.1590/S0103-50532011000600008.

[35] M. Claudel, J.V. Schwarte, K.M. Fromm, New antimicrobial strategies based on metal complexes, Chemistry (Easton) 2 (2020) 849–899, https://doi.org/10.3390/chemistry2040056.

[36] K.L.J.M.P. Nash, Analytical applications of the f-element complexes in solution. Handbook on the Physics and Chemistry of Rare Earths, 1993.

[37] D.F. Peppard, G.W. Mason, J.L. Maier, W.J. Driscoll, Fractional extraction of the lanthanides as their di-alkyl orthophosphates, J. Inorg. Nucl. Chem. 4 (1957) 334–343, https://doi.org/10.1016/0022-1902(57)80016-5.

[38] J. Wang, W. Xu, H. Liu, F. Yu, H. Wang, Extractant structures and their performance for palladium extraction and separation from chloride media: a review, Miner. Eng. 163 (2021) 106798, https://doi.org/10.1016/j.mineng.2021.106798.

[39] P. Tarapcik, Extraction of palladium from nitrate solutions with TBP in tetrachloromethane, Radiochem. Radioanal. Lett. 49 (1981) 353–359.

[40] P. Malik, A. Paula Paiva, Solvent extraction of rhodium from chloride media by *n* , *n* ′-dimethyl- *n* , *n* ′-diphenyltetradecylmalonamide, Solvent Extr. Ion Exch. 26 (2008) 25–40, https://doi.org/10.1080/07366290701784126.
[41] S.S. Kelkar, T.M. Reineke, Theranostics: combining imaging and therapy, Bioconjug. Chem. 22 (2011) 1879–1903, https://doi.org/10.1021/bc200151q.
[42] M. Tosato, M. Asti, M. Dalla Tiezza, L. Orian, D. Häussinger, R. Vogel, U. Köster, M. Jensen, A. Andrighetto, P. Pastore, V. Di Marco, Highly stable silver(i) complexes with cyclen-based ligands bearing sulfide arms: a step toward silver-111 labeled radiopharmaceuticals, Inorg. Chem. 59 (2020) 10907–10919, https://doi.org/10.1021/acs.inorgchem.0c01405.
[43] R. Ruhela, A.K. Singh, B.S. Tomar, R.C. Hubli, Separation of palladium from high level liquid waste – a review, RSC Adv 4 (2014) 24344, https://doi.org/10.1039/c4ra02024c.