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Mechanistic Investigation of Co(II) Extraction by TODGA to Aid Nuclear Forensic Separations

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Abstract — *Nuclear forensic (NF) analysis supports law enforcement inquiries by analyzing evidence tainted with radioactive substances. Separation techniques can be used to identify and quantify actinides and fission products in post-detonation (PD) debris. Environmental transition metals, also present in PD residues, have been observed to impact critical isotope extractions. For example, radio stable cobalt (Co), ubiquitous in urban environments, particularly in corrosion-resistant alloys, paint-drying agents, dyes, and pigments, can impact the separation of important actinides and fission products. The presented work aims to elucidate the chemistry governing Co extraction in samples pertinent to PDNF. Chemistry between Co and N,N,N,‘N’-tetraoctyl diglycolamide (TODGA), the ligand present in the commercial chromatographic resin diglycolamide (DGA), were studied via solvent and chromatographic extraction and spectroscopic analyses. The results indicate that a tetrahedral Co(II) species is extracted by TODGA from highly acidic (>5 M HCl) solutions via a spontaneous entropy-driven reaction. Extraction trends in varied acid concentrations are consistent between solvent extraction and chromatographic extraction methods.*

Keywords — *nuclear forensics, activation product, diglycolamide, extraction, thermodynamics.*

I. INTRODUCTION

Nuclear forensic analysis is critical for the prevention of and response to nuclear smuggling, terrorism, extortion, and arms proliferation [1]. The presence of residual actinides, fission products, and activation products in a sample can aid in identifying the origin of the material being investigated [2,3]. The multitude of elements and the similar size or effective charge of some of the elements present in post-detonation (PD) samples enhances the difficulty of rapid and accurate nuclear forensic separations [4]. Identifying the extraction reaction mechanisms and associated thermodynamic parameters for fission and activation products, such as cobalt, from simplified matrices will promote a fundamental understanding of the extraction chemistry of the system. Characterization of the extraction system will also mitigate the interference of activation products in the extraction of targeted elements. Understanding the extraction chemistry of transition metals is a necessary step to approach the reality of samples collected after a nuclear event.

Separation schemes that target elements from multi-metal sample matrices have been developed using neutral chromatographic resins, such as TRansUranic (TRU) resin and TEtraValent Actinides (UTEVA) resin, and the associated extractants tri-n-butyl phosphate (TBP), octyl phenyl-*N*,*N*-di-isobutyl carbamoyl phosphine oxide (CMPO), and diamyl, amyl phosphonate (DAAP) [5]. The synthesis of diglycolamide (DGA) extractants over the last several

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decades has introduced DGA resins (normal and branched) that are selective for trivalent actinides and lanthanides in high concentrations of HNO_3 and HCl [6,7]. Tetraoctyl diglycolamide (TODGA) is the extractant bound on the DGA normal resin, and the resin exhibits Pu(IV) K_d values 100 times higher than the TRU resin in 0.01 to 3 M HCl [6]. Other features of DGA include a high selectivity for trivalent lanthanides and minor actinides, which warranted its use in the development of several flow sheet processes, including EURO-GANEX, SANEX, and ALSEP [8–10]. TODGA is additionally beneficial in fuel reprocessing schemes because DGAs adhere to the CHON principle, which allows for the minimization of waste through incineration processes [11]. The rapid kinetics displayed for DGA extraction of f-elements and the higher affinity for actinides over the TRU resin indicate promising behavior for uses in nuclear forensic analysis [6,12,13].

Radiochemical separations are commonly accomplished via column chromatography or solvent-extraction practices. Extraction trends of an extractant may be understood using either method, but distribution ratios and elution behavior will vary depending on the method of extraction [14]. The ability to compare characterization methods in both liquid phases makes solvent extraction a more favorable method for the purpose of obtaining fundamental data for applications in nuclear forensics. Ultimately, the extraction mechanism is expected to be consistent across both methods when the system components are constant [15]. The consistent mechanism across the two methods allows solvent-extraction data to provide a guide for designing extraction chromatographic systems used in nuclear forensic applications. In the present work, the solvent-extraction system parameters have been applied to chromatographic experiments to verify consistent trends between methods and establish predictable elution curves for the system.

The literature reports data for the extraction of Co(II) by TODGA from a range of hydrochloric acid (HCl) and nitric acid concentrations using chromatographic methods, but results have differed [6,16]. For example, in HCl media, data reported by Pourmand and Dauphas [16] suggest Co(II) $K_d > 10$ when extracted from ≥6 M HCl, while Horwitz et al. [6] report no extraction of Co(II) from HCl media. In addition, Metwally et al. [17] found that the extraction trends via the solvent method were more consistent with chromatographic trends reported by Pourmand and Dauphas; however, the coordination chemistry of Co(II) was not taken into consideration when defining the extraction mechanism via solvent extraction. The present work investigates the mechanism by which Co(II) is extracted by TODGA through spectroscopic and slope analyses to clarify the conflicting results from previous analyses and enhance separation data for applications in nuclear forensics.

II. EXPERIMENTAL

II.A. Preparation of Reagents

All chemicals used were reagent-grade or better. Aqueous solutions were prepared with 18 MΩ deionized water (DI H_2O) degassed by a rolling boil for 1 h, cooled, and flushed with nitrogen gas for 15 min. Stock solutions were prepared from 36.5% to 38% (w/w) HCl (ACS, Thermo Fisher Scientific) or 68% to 70% (w/w) nitric acid (HNO_3; ACS, Thermo Fisher Scientific) and standardized with sodium hydroxide solutions (NaOH; ACS, 97%+, ACROS) via titrations to potentiometric endpoint using a Titrator Excellence T5 with a DGi11-SC electrode (Mettler Toledo) or to colorimetric endpoint using a 50-mL PYREX Class A burette and 1% phenolphthalein in ethyl alcohol as indicator. Carrier solutions of 100 mM $CoCl_2 \cdot 6\,H_2O$ (99.9%+ metals basis, Thermo Fisher Scientific) and 100 mM $Co(NO_3)_2 \cdot 6\,H_2O$ (99.9% metals basis, Thermo Fisher Scientific) were prepared gravimetrically and diluted with stock acid solutions. Organic solutions were prepared gravimetrically with *N,N,N,'N'*-tetraoctyl diglycolamide (TODGA, 97%, Marshallton Research Laboratories) and diluted with toluene (ACS grade, Thermo Fisher Scientific).

II.B. Batch Solvent Extractions

Organic solutions of 10 to 100 mM TODGA in toluene were preconditioned with equal volumes of acid solutions immediately prior to extraction. The concentration of acid used during pre-equilibration was equivalent to the concentration of acid used during extraction. Equal volumes of aqueous and preconditioned organic phase were added to 8 mL borosilicate glass vials and spiked with 10 µL of $^{59}Co/^{60}Co$ carrier/radiotracer solution (1 to 2.5×10^2 Bq) to obtain a total Co concentration of 12.75 mM in each vial. All vials were sealed with screw-top caps and wrapped in parafilm to prevent leakage. Samples were mixed until equilibrium was reached. A multipurpose tube rotator (Thermo Fisher Scientific) was used for sample shaking (25°C ± 1°C, 60 rpm), except for temperature-dependent experiments (25 to 50 ± 1°C; 150 rpm) which used a temperature-controlled shaking water bath (Grant Instruments OLS25 Aqua Pro). Samples used in temperature-dependent experiments were sealed in plastic bags and horizontally secured, fully submerged in a shaker bath. The samples were centrifuged at 4500 rpm for 5 min to separate the phases after equilibration. A 0.5-mL aliquot was transferred from each phase to respective 7-mL plastic snap-capped polyethylene tubes for gamma (γ) counting (Packard Cobra II Auto-Gamma Counter). Each aliquot was counted for 10 min to achieve a <5% error in the reported counting rate. The auto-γ counting method radiometrically measured ^{60}Co presence in each sample, and activity in the sample due to ^{36}Cl was not counted. Sec. II.F further addresses the presence of ^{36}Cl in the samples. The Co concentration in experiments containing only stable Co was quantified in pre- and post-contact aqueous phases via inductively coupled plasma optical emission spectroscopy (ICP-OES, Agilent 5110 SVDV). ICP-OES samples were prepared with 200 μL of aqueous phase solution and 9.8 mL of 2% HNO_3 diluent. Instrument calibration was performed with a range of Co solutions (0.001–100 ppm) prepared gravimetrically from a 999 ± 3-ppm Co standard solution (Agilent ICP-OES single element cobalt standard) and diluted with 2% HNO_3.

II.C. Column Chromatographic Extractions

Eichrom columns of 2 mL bed volume were packed with 0.65 ± 0.05 g of dry DGA normal resin (Eichrom, 50- to 100-μm particle size). The resin-packed columns were conditioned with 10 mL of 2-M HCl, and the flow of liquid through the column was assisted by applying a variable vacuum to achieve a target flow rate of 2 mL per minute. A 2-M acid rinse was chosen due to the poor wetting of DGA resin with 18 MΩ DI H_2O and lower HCl concentrations. After conditioning, 10 mL of a 12.75-mM ^{59}Co/^{60}Co carrier/tracer solution in varying HCl concentrations was loaded onto the column. Columns were stripped with 10-mL 18 MΩ DI H_2O after the load solution fully eluted.

The eluates from the loading and stripping steps were collected, and a 1-mL aliquot was transferred from each eluant sample to respective 7-mL plastic snap-capped polyethylene tubes for γ counting. Each aliquot was counted for 10 min by automatic gamma counting to achieve a <5% error in the reported counting rate.

II.D. Spectroscopic Investigations

II.D.1. UV-Vis Spectroscopy

An Agilent Cary 5000 UV-Vis and NIR spectrophotometer was used in double-beam mode to obtain absorption data of Co under a variety of aqueous and organic conditions to determine the coordination environment of the metal. Background absorption spectra were obtained using both water and concentrated HCl for aqueous samples and 25 mM TODGA in toluene for organic samples. Data were collected using a 1-cm path length quartz cuvette, and a baseline correction was performed in OriginPro 2023.

II.D.2. X-Ray Spectroscopy

X-ray absorption spectroscopy (XAS) measurements were performed at BM6, National Synchrotron Light Source II, Brookhaven National Laboratory. Samples contained 1.0 mL of an organic phase containing 0.1 M TODGA in toluene that had been contacted with 4.2 to 50 mM Co(II) in 8 M HCl. The 1.0-mL sample was placed in a double open-ended XRF cup with microporous film and ventable cap (O-ring) covered with Mylar film on both ends and sealed with Teflon tape. Multiple scan spectra were recorded at the Co-K edge (7709 eV) using dinitrogen filled transmission and four-element Si fluorescence detectors. Energy calibration was performed against a Co foil. A crystal of Si (111) monochromator was used as a monochromator to give a higher photon flux, 2×10^{12} $cm^{-1}s^{-1}$ at 10 keV. X-ray absorption near edge structure (XANES) analysis was performed using Athena and extended x-ray absorption fine structure (EXAFS) analysis was performed using Artemis.

II.D.3. Gamma Spectroscopy

Post-extraction samples containing ^{38}Cl were analyzed by γ-spectroscopy using a high-purity germanium detector (HPGe, Mirion STD P-Type Coaxial Detector GC4018 HPGe with Lynx Digital Signal Analyzer) at a target peak of 1642 keV. Energy and efficiency calibrations corresponding to the same detector geometry as the measured samples were performed with a 10-μCi $^{152/154}$Eu standard.

II.E. Titration Analysis

Proton concentrations were determined through direct colorimetric titration of the solvent extraction aqueous phase using standardized NaOH solutions. Aqueous phase titrations were performed before contact with the organic phase, after pre-contact, after Co extraction, and after back-extraction of Co with 18 MΩ DI H_2O. The 0.5-M NaOH solutions were standardized using 99.5% ACS-grade potassium hydrogen phthalate (KHP). The KHP was dried in an oven at 110°C for 2 to 4 h and stored in a desiccator prior to standardization measurements. HCl solutions with concentrations between 0.01 and 10 M were standardized with a known 0.5-M NaOH solution. The titration data were fit linearly in OriginPro

2023, and the fit, outlined in Eq. (1), was used to verify consistency in the burette titration method. Multiple back-extractions were performed to ensure all acid was removed from the organic phase.

$$\text{Volume NaOH to reach equivalence(mL)} = 10.33 \times [H^+] \quad (1)$$

II.F. Activation Analysis

II.F.1. Activation of ^{59}Co

Co(II) solutions containing radiotracers of ^{60}Co (β/γ, $t_{1/2} = 5.271$ yr) and ^{36}Cl (β, $t_{1/2} = 301\ 000$ yr) for solutions containing chloride were prepared by neutron activation at the University of Florida's 100-kW Argonaut Training Reactor (UFTR) by dissolving 0.4037 g cobalt (II) chloride hexahydrate ($CoCl_2 \cdot 6\,H_2O$, 99.9% metals basis, Thermo Fisher Scientific) or 0.2449 g cobalt (II) nitrate hexahydrate ($Co(NO_3)_2 \cdot 6\,H_2O$, 99.9% metals basis, Thermo Fisher Scientific) in 1 mL 18 MΩ DI H_2O. The metal salt solutions were heat-sealed in 2-mL polyethylene vials, and each 2-mL vial was nested in a 20-mL polyethylene vial. Samples were irradiated for 10 min under the approximate thermal and epithermal neutron flux of $2 \times 10^{12}\ \frac{\text{neutrons}}{\text{cm}^2\text{s}}$ and $1 \times 10^{11}\ \frac{\text{neutrons}}{\text{cm}^2\text{s}}$, respectively. Aliquots of the stock were analyzed by γ-spectroscopy with a Packard Cobra II Auto-Gamma Counter and a Beckman LS-6500 Liquid Scintillation Counter. Analysis on the auto-γ counter confirmed that the radioactivity was primarily due to ^{60}Co ($7.4 \times 10^4 - 2.6 \times 10^5$ Bq/mL).

II.F.2. Activation of ^{35}Cl and ^{37}Cl

The high neutron cross-section of stable chlorine isotopes, ^{35}Cl (75.76% abundance, $\sigma_\gamma = 43.6$ b) and ^{37}Cl (24.24% abundance, 0.38 b) makes neutron activation analysis a viable option for quantification of the chloride concentration in post-extraction samples [18]. Solutions containing ^{38}Cl (β/γ, $t_{1/2} = 38$ min) and ^{36}Cl (β, $t_{1/2} = 301\ 000$ yr) were prepared by neutron activation at the UFTR by dissolving known quantities of NH_4Cl (99.6%, Thermo Fisher Scientific) in 1 mL 18 MΩ DI H_2O to prepare five solutions at a range of Cl concentrations between 10 and 50 mM. In addition, solvent extraction experiments were performed as previously described using stable 12.75-mM $CoCl_2$, and the loaded organic phase samples were back-extracted into 18 MΩ DI H_2O to quantify the concentration of chloride involved in the extraction reaction. A back-extraction of the pre-conditioned organic phase, where TODGA was contacted with HCl only, was performed to analyze the uptake of acid by TODGA without the presence of Co(II) in the system. The 1-mL NH_4Cl solutions and 1-mL aliquots of aqueous phase extraction samples were individually prepared in 2-mL polyethylene vials and heat-sealed. Samples were irradiated for 10 min at 25 kW under the approximate thermal and epithermal neutron flux of $2 \times 10^{12}\ \frac{\text{neutrons}}{\text{cm}^2\text{s}}$ and $1 \times 10^{11}\ \frac{\text{neutrons}}{\text{cm}^2\text{s}}$, respectively. Ammonium chloride samples were used to create a calibration curve to relate known ^{38}Cl concentration to activity. All measurements were performed under the same geometry, and the activity of activated ^{60}Co (photopeaks at 1173 keV and 1333 keV) and ^{60m}Co (photopeak at 58.6 keV) in the samples did not interfere with the 1642-keV photopeak used for ^{38}Cl analysis [19]. Stoichiometric ratios were determined through a comparison of mole Cl to mole Co in the back-extracted solutions. Co(II) concentration was determined prior to activation through ICP-OES.

II.G. Extraction Equilibria Treatment

The selective extraction of metals in aqueous solutions by TODGA is expected to follow a solvation mechanism for which the general reaction is outlined in Eq. (2), where M^{m+} is the metal cation, X^- a monovalent anion, and H^+ a proton. The organic phase is denoted by the accent bar above a particular species. Solvation of the metal complex for organic phase uptake requires the formation of a neutral metal-ligand complex prior to coordination with solvating extractants such as TODGA [20]. TODGA uptake of molecular acid, primarily HNO_3, has been reported [21–23].

$$M^{m+} + hH^+ + xX^- + \overline{nTODGA} \rightleftharpoons \overline{MH_iX_k \cdot (HX)_j \cdot TODGA_n} \quad (2)$$

$$\text{Where } m = k - i,\ h = i + j, \text{ and } x = k + j$$

The Co predominantly exists as the divalent ion Co^{+2} in acidic solutions [24,25]. Solvent extraction by the solvation mechanism yields two related values: the extraction equilibrium constant (K_{ex}) and the metal distribution ratio (D_M). K_{ex} is defined in Eq. (3), while D_M, shown in Eq. (4), provides a method for quantifying the extraction of metal through a ratio.

$$K_{ex} = \frac{\overline{MH_iX_k \cdot (HX)_j \cdot TODGA_n}}{[M^{m+}][X^-]^x[H^+]^h[\overline{TODGA}]^n} \quad (3)$$

$$D_M = \frac{[\overline{M}]}{[M]} \frac{\overline{MH_iX_k \cdot (HX)_j \cdot TODGA_n}}{[M^{m+}]} \qquad (4)$$

The distribution ratio and extraction constant are mathematically related through Eq. (5). A regression plot of log(D) versus log[TODGA] and log[X] can indicate the stoichiometric coefficient (n or x) for TODGA and the monovalent anion. Quantification of K_{ex} from Eq. (5) is possible once stoichiometric coefficients are established for all components of Eq. (2).

$$\mathrm{Log}(D_{Co}) = n\ \log[TODGA] + \log K_{ex} + m\ \log[Cl^-] + h\ \log[H^+] \qquad (5)$$

Extraction of a metal by TODGA on a resin support is determined through K_d, which compares the total concentration of metal sorbed onto the resin to the concentration of metal remaining in the solution. K_d is defined by Eq. (6), where C_B and C_A are the total concentration of metal in the aqueous phase before and after extraction, respectively; w is the weight of the dry resin; and v is the volume of aqueous solution.

$$K_d = \frac{C_{solid}\ \text{per g TODGA}}{C_{solution}\ \text{per mL solution}} = \frac{\frac{(C_B - C_A)}{w}}{\frac{C_A}{v}} \qquad (6)$$

The thermodynamic parameters of the solvent extraction reaction can be determined by applying the extended, linear form of the van't Hoff equation as given by Eq. (7), where R is the universal gas constant and T refers to the temperature in kelvin. Indirect quantification of ΔH and ΔS for the overall extraction reaction was achieved by quantifying $\ln(K_{ex})$ at variable temperatures. The overall solvent extraction reaction [Eq. (2)] includes the metal dehydration, complexation of the metal with TODGA, and the transition of the complex across the phase boundary. The temperature variation method has been used for thermodynamic analysis of solvent extraction systems with success [26,27]. Quantification of the ΔG of the overall reaction was calculated as given by Eq. (8).

$$\ln(K_{ex}) = \left(\frac{-\Delta H}{R}\right)\frac{1}{T} + \frac{\Delta S}{R} \qquad (7)$$

$$\Delta G = -RT\ \ln(K_{ex}) \qquad (8)$$

Experimental uncertainties associated with the reported values were calculated by propagation of error in pipette calibrations, counting statistics, and standard deviation of replicate measurements. Uncertainty is reported to 2σ.

III. RESULTS AND DISCUSSION

III.A. Coordination of the Extracted Complex

The time to reach equilibrium in Co(II) extraction reactions was quantified prior to any further analysis. Results indicate that the system reaches equilibrium within 1 to 5 min when using the shaker required for Q7 temperature-controlled experiments (Fig. SI1). All sam- Q8 ples were shaken for a minimum of 5 min to ensure equilibrium was reached in the system prior to analysis. Extraction of Co(II) by TODGA was investigated in systems with different organic phase diluents in addition to equilibration time. The diluents tested were dodecane, hexane, toluene, and trichloroethylene. TODGA was diluted in four diluents with different functional groups and the extraction of Co(II) by TODGA in each solution was quantified. TODGA diluted in toluene produced the highest extraction of Co(II) (Table SI1); toluene was used Q9 as the organic phase diluent in all subsequent experiments.

Co(II) extraction trends in varied concentrations of acid were experimentally determined for HNO_3 and HCl systems via solvent extraction. Co(II) is extracted by TODGA from concentrations of HCl greater than 5 M, as presented in Fig. 1. The extraction increases with increasing acidity up to 8 M HCl. The observed trend in Fig. 1 is consistent with previously reported extraction trends [17]. In contrast, Co(II) remains in the aqueous phase in all concentrations of nitric acid.

Co(II) can undergo a high-spin electronic configuration dictated by the metal's ligand field and geometry, thus determining a tetrahedral or octahedral coordination of the metal with surrounding ligands [28]. Changes in aqueous Co(II) coordination were observed in the visible spectrum as the concentration of HCl in solution increased, as evidenced by Fig. 2. Co(II) adopts an octahedral geometry as $[Co(H_2O)_6]^{2+}$ and absorbs light at a wavelength of 525 nm in low-acid solutions (0–4 M HCl), while the tetrahedral complex, $CoCl_4^{2-}$, persists at high acidities (7–12 M HCl), with a peak absorbance of 680 nm. The Co(II) in solutions of 5 M and 6 M HCl exhibit peak absorbance at both wavelengths of interest, which can be attributed to a mixed speciation of the metal in the solutions.

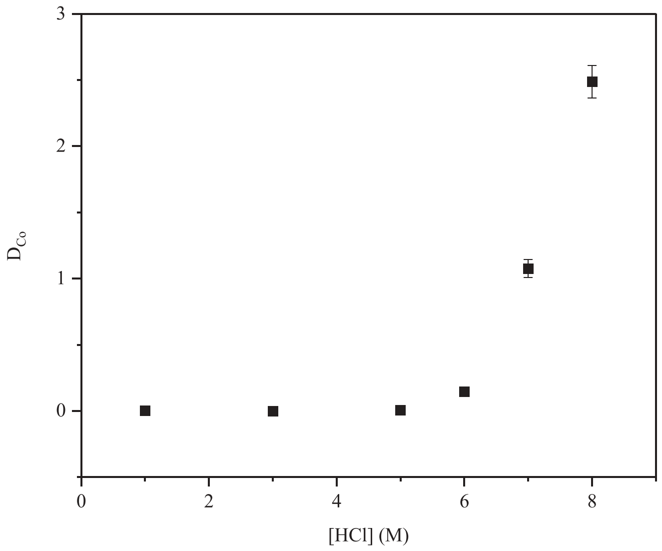

Fig. 1. D_{Co} versus HCl concentration (M) with conditions: 12.75 mM Co(II)/0.025 M TODGA/toluene at 25°C ± 1°C. Errors are 2σ from triplicates.

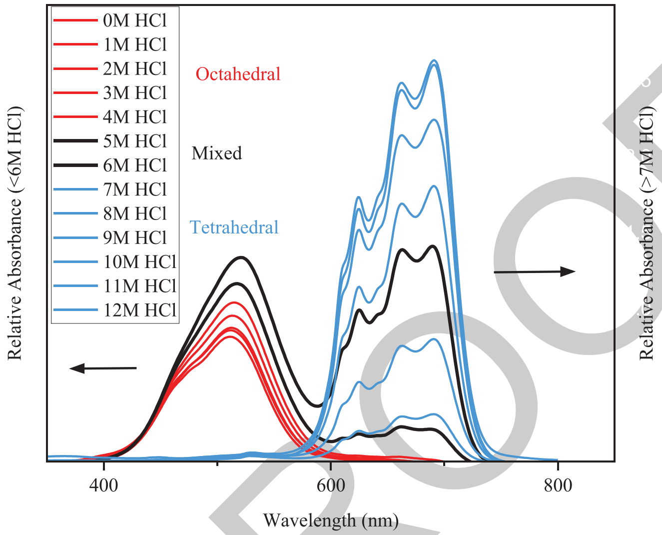

Fig. 2. Absorbance spectra of 60 mM Co(II) (left axis) and 4.2 mM Co(II) (right axis) in varied concentrations of HCl from 0 to 12 M in increments of 1 M.

TODGA extraction trends for Co(II) in HCl can then be explained by the metal coordination. Fig. 1 indicates that TODGA is selective for the tetrahedral $CoCl_4^{2-}$ species. The same tetrahedral complex is present in both a pre-contact aqueous phase and a loaded organic phase, Q10 as confirmed via UV-Vis (Fig. SI2). Selectivity of TODGA for tetrahedral $CoCl_4^{2-}$ justifies the lack of Co(II) extraction at lower HCl concentrations as well as in the nitric acid system where the $[Co(H_2O)_6]^{2+}$ species predominates. The UV-Vis spectra of Co(II) in 0 to 15 M HNO_3 solutions confirm an octahedral coordinated species is present across the acid concentration range (Fig. SI3). Q11

XANES spectroscopy also indicates the presence of a tetrahedral coordinated Co(II) extracted species in 8 M HCl. The near edge of 4.2 to 50 mM Co(II) extraction spectra (~7709 eV) shown in Fig. 3 produced strong pre-edge features matching the tetrahedral $CoAl_2O_4$ standard. The EXAFS analysis for the extracted 4.2 mM Co with 100 mM TODGA from 8 M HCl provides relevant structural information about the cobalt environment. The EXAFS data are presented in Fig. 4, with the loaded organic phase data presented in Black and a tetrahedral fit line in red. The fitting parameters, presented in Table 1 , show a coordination number (CN) of 4 for Co-Cl bonds, indicating a tetrahedral arrangement around the cobalt ion, which aligns with coordination geometries observed in similar complexes. The bond distance of 2.29 Å for Co-Cl is consistent with previously reported values for $CoCl_4^{2-}$ complexes [29]. This suggests a coordination between the cobalt and chloride ligands, with $CoCl_4^{2-}$ as the Co(II) extracted species.

The stoichiometric coefficient of TODGA involved in the extraction reaction was quantified by plotting log[TODGA] versus $\log D_{Co}$. The linear regression with a slope of 2.0 ± 0.1 presented in Fig. 5 suggests that two TODGA molecules are associated with each extracted Co(II) in the organic phase complex.

The stoichiometric coefficients for the monovalent ions in the extraction system, H^+ and Cl^-, were quantified through titration analysis and neutron activation analysis,

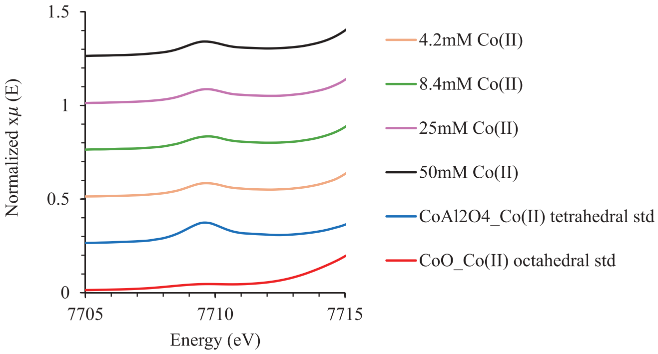

Fig. 3. Normalized XANES region of extracted Co(II) from 100 mM TODGA by 8 M HCl. The Co(II) tetrahedral standard was $CoAl_2O_4$ and the octahedral standard was CoO. The near-edge of 4.2 to 50 mM Co(II) extraction spectra (~7709 eV) produced strong pre-edge features matching the tetrahedral standard. XANES analysis suggests the presence of a tetrahedrally coordinated Co(II) extracted species in 8 M HCl. Extraction conditions: (O) 0.1 M TODGA in toluene; (A) 4.2 to 50 mM Co in 8 M HCl.

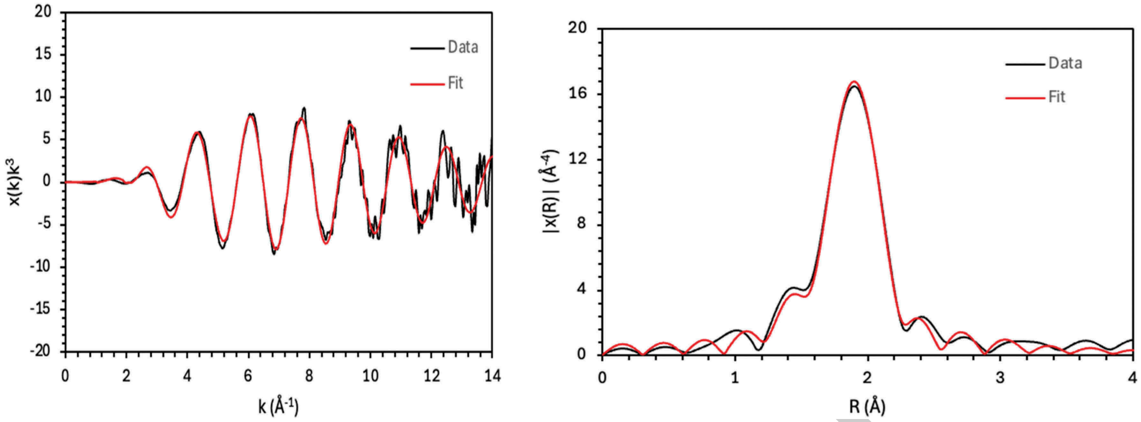

Fig. 4. Fitted k^3-EXAFS spectra and Fourier transform of 4.2 mM Co(II) in 100 mM TODGA and 8 M HCl. Experimental data are shown in Black and EXAFS fits are shown in red. Similar spectra were found for all concentrations used (4.2 to 50 mM). Extraction conditions: (O) 0.1 M TODGA in toluene; (A) 4.2 to 50 mM Co in 8 M HCl.

TABLE 1

EXAFS Fit Parameters Obtained for Loaded Organic Phase

Bond	CN	R (Å)	σ^2 (Å^2)
Co-Cl	4.09 ± 0.21	2.29 ± 0.02	0.003 ± 0.0005

[a] S_0^2 fixed at 0.85; k space data range for Fourier transform: 2–12.891 Å; R space curve fitting range: 1–3 Å.
Extraction conditions: (O) 25 mM TODGA in varied diluent; (A) 12.75 mM Co(II) in 8 M HCl.

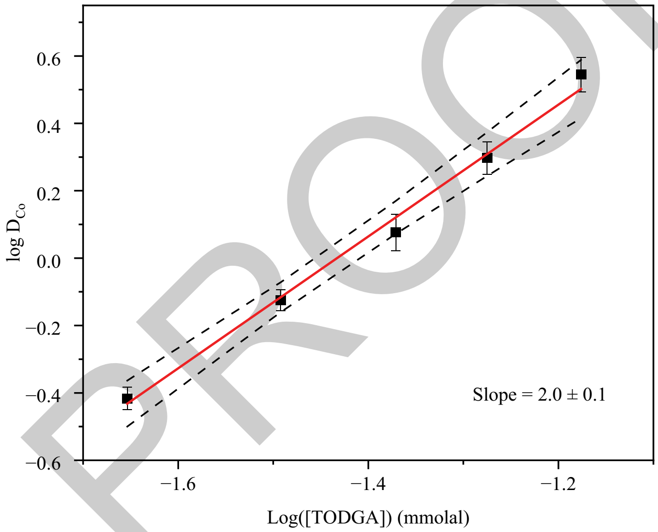

Fig. 5. Log(D_{Co}) versus log[TODGA] from the extraction system: (O) 0.02 to 0.07 mmolal TODGA in toluene; (A) 6.65 mmolal Co in 9 molal HCl at 25°C ± 1°C. The solid red line illustrates a linear fit on the data, while the dashed Black lines represent a 95% confidence band relative to the fit.

respectively. Both analysis methods were applied to the aqueous phase samples obtained by back-extracting the loaded organic phase into DI H_2O. The stoichiometric coefficients were determined by comparing the concentration of Cl^- or H^+ to that of Co(II). Table 2 reports the experimentally determined ratios of TODGA, Cl^-, and H^+ to Co(II), respectively. The 2:1 TODGA:Co ratio, determined through slope analysis in Fig. 5, was confirmed with ICP-OES measurements of back-extracted aqueous solutions prior to titration analysis. The ratio of Cl^-:Co was experimentally quantified via neutron activation analysis of ^{38}Cl, and results indicate that 5 ± 0.5 chloride ions are extracted for every one Co(II) ion. Of the five total extracted chloride ions, four are coordinated to Co(II) in the inner sphere of the extracted

TABLE 2

Mol Ratio Comparison of Post-Extraction Organic Phase Species

Species	Mol Ratios
TODGA:Co	2 ± 0.1
Cl^-:Co	5 ± 0.5
H^+:TODGA:Co	2–6:2:1
Neutral Co Species	$CoCl_4H_2$

Extraction conditions: (O) 25 mM TODGA in varied diluent; (A) 12.75 mM Co(II) in 8 M HCl.

complex, as evidenced by UV-Vis and XAS results. The remaining chloride ion is extracted as molecular HCl by TODGA directly [23]. Colorimetric titrations confirmed a H^+:Co ratio of 3.8 (±1.8):1 in the extracted complex. It is expected that three protons are present in the complex based on the notion that TODGA targets neutral species in the aqueous phase. UV-VIS and XAS determined that the tetrahedral $CoCl_4^{2-}$ is the dominant cobalt species present under highly acidic conditions at which extraction is successful in this system. Therefore, two protons are anticipated to coordinate with the tetrahedral aqueous complex during extraction to balance the anionic charge. The coordinated protons are presumed to neutralize the tetrahedral chloride complex making solvation of the complex by TODGA favorable; however, the exact coordination of the protons in the cobalt complex is not well established. The third proton resides with the molecular HCl extracted by TODGA directly. Combining the stoichiometric ratios and coordination data obtained thus far, the extracted complex can be represented by the expression:

$$CoCl_2 + 3HCl + \overline{2TODGA} \rightleftharpoons \overline{CoCl_4H_2 \cdot TODGA_2 \cdot (HCl)} \tag{9}$$

It is necessary to note the possibility of the formation of two product species, $\overline{CoCl_4H_2 \cdot TODGA}$ and $\overline{(HCl) \cdot TODGA}$, rather than the singular, larger product $\overline{CoCl_4H_2 \cdot TODGA_2 \cdot (HCl)}$. Differentiating between the formation of $\overline{CoCl_4H_2 \cdot TODGA}$ and $\overline{(HCl) \cdot TODGA}$ and the formation of a singular larger species $\overline{CoCl_4H_2 \cdot TODGA_2 \cdot (HCl)}$ in the organic phase require more extensive computational analyses.

III.B. Thermodynamics of the Extraction Reaction

The thermodynamics of the overall extraction reaction were quantified to address reaction favorability for applications in multi-element separations. Fig. 6a compares log[TODGA] to $\log D_{Co}$ at variable temperatures between 25°C and 50°C; the linear regression was applied to determine $\ln K_{ex}$ at each temperature. The average slope across the temperature range was 2.0 ± 0.3, indicating that the coordination environment does not change due to temperature. Fig. 6b exhibits the van 't Hoff plot in which the linear regression of null slope indicates $\ln K_{ex}$ is independent of temperature between 25°C and 50°C.

The thermodynamic parameters derived from the van 't Hoff plot [Fig. 6b data input in Eqs. (7) and (8)] indicate that the reaction is an entropically driven spontaneous process over the analyzed temperature range, consistent with reported data for the system [17]. The enthalpy, entropy, and Gibbs free energy terms are presented in Table 3. The results align with thermodynamic trends reported for TODGA extraction reactions with other metals [30]. For example, Dutta et al. [30] compared conditional extraction equilibria for TODGA systems that form tri-solvate complexes, Y(III), to systems that form tetra-solvate complexes, Am(III). Their data indicate that enthalpy values are less negative for the tri-solvate complexes as compared to the tetra-solvate ones [30]. The results herein continue the trend in reporting

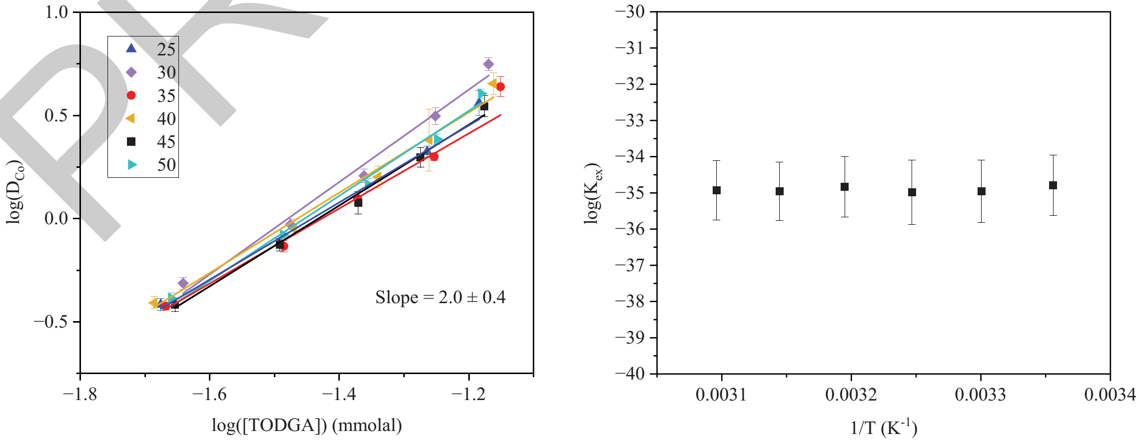

Fig. 6. (a) Log(D_{Co}) versus log[TODGA] at 25°C ± 1°C to 50°C ± 1°C (left) (b) van 't Hoff plot of ln (K_{ex}) versus 1/T for the determined Co(II)-TODGA complex (right). Extraction conditions: (O) 0.02 to 0.07 mmolal TODGA in toluene; (A) 6.65 mmolal Co in 9 molal HCl.

TABLE 3

Thermodynamic Parameters Governing Co(II) TODGA Extraction at 298 K

ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol·K)
−85 ± 9	~0	280 ± 10

Extraction conditions: (O) 25 mM TODGA in toluene; (A) 12.75 mM Co(II) in 8 M HCl.

a less negative enthalpy value for the di-solvate Co-TODGA complex as compared to the reported tri-solvate Y-TODGA complex in an HCl system. Therefore, it is possible that the number of solvates coordinated in the extracted complex directly contributes to the change in enthalpy of the overall reaction, with a higher ion solvation, contributing to a more negative change in enthalpy of reaction. Further analysis of this trend with more elements is necessary to verify this claim.

III.C. Chromatographic Extraction

Solvent extraction data regarding the system's mechanism of extraction and overall reaction thermodynamics are relevant for predicting extractant selectivity in multi-element sample matrices such as samples investigated for nuclear forensics. However, column chromatography is the primary method for elemental quantification of nuclear forensic samples due to high separation factors, simplicity of operation, and high chemical yield [1,31]. While the methods are typically understood to elicit comparable selectivity trends, Co(II) extraction trends using the DGA resin are inconsistent in the literature [6,16]. Extraction results from Pourmand and Dauphas using the DGA resin indicate an increase in extraction with increasing concentration of acid after 6 M HCl and $K_d \sim 80$ in 9 M HCl [16]. The extraction of Co(II) by TODGA on a resin support as reported by Horwitz *et al.* indicates $K_d < 2$ in all concentrations of HCl [6]. Fig. 7 exhibits extraction of Co from varied concentrations of HCl using the DGA normal resin and clarifies previously reported results by comparing trends between extraction methods. The extraction trend in Fig. 7 matches that in Fig. 1, indicating consistency between the two extraction methods for the system and an agreement with data reported by Pourmand and Dauphas [16].

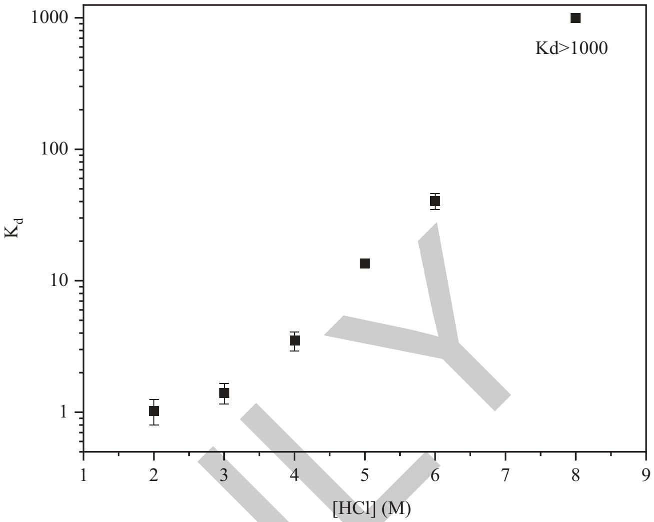

Fig. 7. K_d versus [HCl]. Batch extraction conditions: 12.75 mM Co(II) in 2 to 8 M HCl with 0.65 g DGA resin. Errors are 2σ from triplicates.

IV. CONCLUSION

The work demonstrates that Co(II) in the tetrahedral form is extracted by TODGA from aqueous solutions of high acidity (>5 M HCl) via solvent and chromatographic extraction. Investigation of extraction trends with the resin is relevant for nuclear forensic separations, which employ commercially available resins such as DGA. The current work served to verify consistency between methods and address conflicting trends in the existing literature regarding Co(II) extraction. The overall extraction reaction is entropy-driven and can be represented by the reaction $CoCl_2 + 3HCl + \overline{2TODGA} \rightleftharpoons \overline{CoCl_4H_2 \cdot TODGA_2 \cdot (HCl)}$. Mechanistic and thermodynamic trends on the extraction reaction will aid the development of models for rapid separations. Coordination and complexation data of other activation and fission products can be used to strengthen artificial intelligence and machine learning algorithms to enhance predictions for multi-metal separations in nuclear forensics.

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Author Contributions

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Disclosure Statement

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Supplementary Material

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