HIGH YIELD FISSION PRODUCT SEPARATIONS AND QUANTIFICATION
FOR NUCLEAR FORENSIC APPLICATIONS

By

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To the Faculty of Washington State University:

The members of the Committee appointed to examine the dissertation of KEVIN JOHN SWEARINGEN find it satisfactory and recommend that it be accepted.

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HIGH YIELD FISSION PRODUCT SEPARATIONS AND QUANTIFICATION FOR NUCLEAR FORENSIC APPLICATIONS

Abstract

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Strontium-90 and its daughter, yttrium-90, have cumulative fission yields of approximately 6 percent from the thermal neutron induced fission of uranium-235. With these high yields, Sr and Y are prevalent following an accidental release or a nuclear detonation. Strontium-90 has a half-life of 28.8 years; accordingly, both it and $^{90}$Y will continue to be present in the environment for several centuries following a release. The relatively long half-life and high yields make $^{90}$Sr and $^{90}$Y useful isotopes for nuclear forensics. Due to chemical similarities, ingested $^{90}$Sr can replace Ca within the structure of bone, leading to an increased health risk. The long half-life and health risk requires $^{90}$Sr environmental monitoring for public health concerns. Due to $^{90}$Sr and $^{90}$Y being quantified by their $\beta^-$ emissions, traditional quantification methods require substantial separations or wait times (approximately 3 weeks) before quantification can be completed. In both public health and nuclear forensics, lengthy wait times for accurate quantifications are never desirable.

This body of work characterizes separation techniques and develops improved quantification methods for Sr and Y. Solid phase extractions are typically utilized for the quantification of $^{90}$Sr and $^{90}$Y in case public health and nuclear forensics monitoring. The two primary commercial Sr resins were compared
under identical conditions to gauge which product was the most effective at isolating Sr. Improved novel use of inductively coupled plasma optical emission spectrometry techniques were developed to improve quantification methods for complex solutions without increasing sample processing time or costs. A new technique was developed to simultaneously determine $^{90}$Sr and $^{90}$Y activities via liquid scintillation counting to reduce the time required to obtain the individual activities from 3 weeks to 1 week without a decrease in precision.
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Neutron induced fission of uranium results in a 2 peaked distribution curve, such as the cumulative yields for thermal neutron induced fission of $^{235}$U shown in Figure 1.1. Cumulative yield indicates that the yield percentage includes all of the shorter lived isotopes that eventually decay to that specific isobar or isotope. The dashed line in Figure 1.1 shows the 90 isobar, which has an independent yield of 5.8 percent.\(^1\) Within the 90 isobar, the two longest long lived unstable isotopes are $^{90}$Sr and $^{90}$Y, with cumulative yields of approximately 6 percent; $^{90}$Sr has a half-life of 28.8 years and $^{90}$Y has a half-life of 2.67 days.\(^2\) The decay path of $^{90}$Sr and $^{90}$Y to stable $^{90}$Zr is shown in Figure 1.2. The much longer half-life of the parent, $^{90}$Sr, compared to the daughter, $^{90}$Y, leads to secular equilibrium occurring. Given a sample of pure $^{90}$Sr, $^{90}$Y ingrowth occurs and after approximately 6 half-lives of $^{90}$Y, the activity of $^{90}$Sr equals that of $^{90}$Y. If the system is undisturbed, the activities will continue to be equal until all of the $^{90}$Sr has decayed.\(^3\)

The 28.8 year half-life of $^{90}$Sr makes it a problematic isotope for environmental contamination. It is too long of a half-life for it to simply decay away without causing issue, while still being short enough to cause problems due to its (and its daughter’s) specific activities. Even with the Limited Test Ban Treaty and the Comprehensive Test Ban Treaty limiting nuclear detonations, children’s baby teeth still had measureable quantities of $^{90}$Sr in 1996.\(^4\)\(^6\)
Figure 1.1. Independent yields for the mass distribution of thermal neutron induced fission of $^{235}$U. The dashed line marks the 90 isobar.

Figure 1.2. Decay path of $^{90}$Sr and $^{90}$Y and to stable $^{90}$Zr.
Strontium-90 is an important isotope for environmental monitoring because Sr can replace Ca in bone. The 546 keV $\beta^-$ decay of $^{90}\text{Sr}$ and the 2.281 MeV $\beta^-$ decay of $^{90}\text{Y}$ causes $^{90}\text{Sr}$ to be an important isotope for public health. If $^{90}\text{Sr}$ is ingested, a majority of it will be incorporated into the structure of bones and teeth. The incorporation of stable Sr has negligible effects but the radioactive decay of $^{90}\text{Sr}$ and then $^{90}\text{Y}$ makes it a serious health concern. The emission of high energy beta particles from $^{90}\text{Sr}$ and $^{90}\text{Y}$ from within the bone drastically increases the risk of cancer forming in the bone, bone marrow, and the soft tissue surrounding the bone. The serious repercussions of $^{90}\text{Sr}$ ingestion led the EPA to set the maximum permissible concentration of $^{90}\text{Sr}$ in drinking water at 8 pCi/L ($6\cdot10^{-16}$ M). As such, it is an isotope that should be monitored to prevent health issues and subsequent legal ramifications.

In addition to being a concern for public health, the 90 isobar, specifically $^{90}\text{Sr}$ and $^{90}\text{Y}$, is important for nuclear forensics. The 90 isobar is located on the left shoulder of the first peak in the fission product curve shown in Figure 1.1. At this location, there are shifts in yield percentage from changes in both the target nucleus and the energy of the neutron. Figure 1.3 shows some of the shifts that can occur when the incident neutron energy (A) or the target nuclei (B) are changed. For $^{235}\text{U}$, as the incident neutron energy is increased, there is a slight increase in yield percent for the 90 isobar. In the case of the target nucleus, as it gets heavier ($^{235}\text{U} \rightarrow ^{238}\text{U} \rightarrow ^{239}\text{Pu}$), the yield percentage gradually decreases. The change in yields for the 90 isobar leads to changes in ratios between $^{90}\text{Sr}$ and other fission products, which can then be used to deduce details about the original fission event that led to the release of the radioisotopes.
Due to the relatively long half-life of $^{90}\text{Sr}$, it is very useful for monitoring for nuclear safeguards and nuclear forensics. The 28.8 year half-life means that it is still measurable, even in the Trinitite samples from the first nuclear test.\textsuperscript{2,8} Strontium-90 measurements are not only limited to post-detonation forensic studies. The ratios can be used for pre-detonation nuclear forensics as well. In pre-detonation nuclear forensic studies, the sample may be spent nuclear fuel or radioactive sources. In either case, the goal is a potential dirty bomb or for the nuclear fuel, to extract nuclear material to create an atomic bomb. In the pre-detonation studies, the isotopic ratios between $^{90}\text{Sr}$ and other isotopes can be used to determine the source of the radioactive material, its age, and what the type of reactor it came from.\textsuperscript{9-12}
Motivation for Research

The motivation for this research is to develop improved separation and quantification techniques for Sr and Y in order to better characterize the environmental fractionation and transport following the release of Sr and/or Y into the environment. Whether the measurements are for environmental health and safety or nuclear forensics, expeditious results are crucial. In the case of elemental characterization, the current methodologies require front-end processing before a simple elemental analysis can be done if the sample is in a more complicated matrix such as seawater or brine. In the case of organic solutions, the organic solvent typically is removed or digested and then the metals are brought up in an aqueous solution for analysis. Current techniques that remove the need for front-end sample processing or digestion typically require specialized add-ons to the instrument that are not on standard set-ups. Because $^{90}\text{Sr}$ is a pure beta emitter and $^{90}\text{Y}$ has a $1.4 \times 10^{-6}\%$ branching ratio for its gamma emission, both are typically quantified by their $\beta^-$ decay. Many techniques require the separation of $^{90}\text{Sr}$ and $^{90}\text{Y}$ and/or waiting on the ingrowth of $^{90}\text{Y}$. As is the case with the elemental analyses, this is a time consuming step, in the case of ingrowth, it can take 18 days to achieve secular equilibrium.

This body of work is composed of three primary studies on the separation and quantification of Sr and Y using traditional laboratory techniques and instrumentation. In addition, several secondary studies on improved analytical techniques were performed in support of the primary studies.

The first primary study focuses on the comparison of two solid phase extraction techniques for the isolation of Sr from similar elements such as Ba. In both nuclear forensics and environmental studies, solid phase extraction resins are commonly used. Because $^{90}\text{Sr}$ is a pure $\beta^-$ emitter, all impurities must be removed prior to radiometric analysis. The specific motivation of this study was to compare the two “name-brand” solid phase extraction resins for Sr. Both resins are commonly used for environmental samples containing Sr, but there was no direct comparison of the two resins’ separation abilities. This
study directly compares the two resins under identical conditions and determines which resin provides optimum separations.

The second primary study develops techniques for the elemental analysis of non-traditional solutions using a traditional Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) set-up with minimal additions. This study was a collaborative study done with Trevor Omoto and had two primary objectives. The first objective was to develop analytical techniques for the quantification of samples (with no front-end processing) in neutral and high salt solutions. The second objective was to develop methodology for the analysis of a number of metals in organic solvents. These techniques required minimal additions, in terms of both cost and components, to a traditional ICP-OES and accordingly, are readily available to any laboratory that has an ICP-OES. The use of these methods decreases the sample processing time and removes the need for radiotracers for solvent extraction studies.

The final primary study is the development of a new liquid scintillation counting (LSC) technique for solutions containing $^{90}$Sr and $^{90}$Y. Typically when a solution contains $^{90}$Sr and $^{90}$Y, LSC counting is postponed until secular equilibrium has been achieved since the $\beta^-$ energy distributions for $^{90}$Sr and $^{90}$Y are difficult to resolve with LSC. This technique utilizes an equation derived from the original Bateman equation and relies on the change in activity over the course of several days, which is then fit to a derivation of the Bateman equation. When the sample consists of only $^{90}$Sr and $^{90}$Y, the change in activity is directly related to the ratio of the two isotopes. A curve fitting program is used to determine the ratios based off the change in activities over the course of several days. This drastically decreases the time required for quantification, from approximately three weeks, down to as little as several days.
A number of secondary studies were performed in addition to the primary studies. The interaction of Sr with environmental colloids and the characterization of the colloids were investigated for more direct applications to environmental systems. Alongside this, a solvent extraction study was performed in order to examine the efficacy of solvent extractions at neutral pH for environmental stability constant determinations. As these studies were run parallel with, rather than under the scope of this body of work, they were included as appendices. Several other appendices are included which cover the specifics of the instrumental and laboratory techniques used in order to achieve this body of work.
References


CHAPTER 2
BATCH COMPARISONS OF STRONTIUM AND BARIUM RETENTION AND CAPACITIES ON ANALIG® SR-01 AND EICHROM SR RESINS

Preface
This work was originally performed as an investigation into options available for isolating $^{90}\text{Sr}$ from a mixture of fission products. Strontium-88 has a relatively small thermal neutron capture cross-section (5.8 mb), especially when compared with the other stable Sr isotopes (0.82 b for $^{86}\text{Sr}$ and 17 b for $^{87}\text{Sr}$). The majority of the neutron capture that would occur would be $^{87}\text{Sr} (n,\gamma)^{88}\text{Sr}$. With these cross sections, neutron activation did not appear to be a viable method for obtaining a Sr radiotracer. Strontium-90 has a high fission yield (approximately 5%) with a half-life of 28.8 years. The use of an exchange resin provides a means to both isolate Sr from the other fission products and act as a generator for $^{90}\text{Y}$. When $^{90}\text{Sr}$ is retained on the resin, $^{90}\text{Y}$ (half-life of 64 hours) will grow in as $^{90}\text{Sr}$ decays. The two elements have different charges (+2 and +3) and are relatively easy to separate one from another, especially if specific ligands are used during the extraction. Barium was selected as the element to gauge the efficacy of the selected resins, as Ba features a similar cumulative fission yield to $^{90}\text{Sr}$, the same oxidation state, and very similar ionic radii (1.4-1.6 Å for Ba and 1.2-1.4 Å for Sr). If a resin can isolate Sr from Ba, then separating Sr and Y in a generator role should not be present a problem.

The following chapter has been published as an article in the journal Solvent Extraction and Ion Exchange. The copyright information is detailed in Appendix G.
**Batch Comparisons of Sr and Ba Retention and Capacities on Analig® SR-01 and Eichrom Sr Resins**

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Department of Chemistry, Washington State University, Pullman, WA, USA

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**Abstract**

The isolation of strontium from aqueous media may be required for environmental monitoring or nuclear forensics sample analyses. The prevalent method is to use a strontium selective extraction chromatographic resin. Two such products are Eichrom Technologies Sr resin and IBC Advanced Technologies AnaLig® Sr-01 resin. Eichrom Technologies Sr resin utilizes a crown ether (4,4′(5′)-di-t-butylecyclohexano-18-crown-6) diluted in 1-octanol and coated onto Amberchrom™ CG71 resin, and IBC Advanced Technologies AnaLig® Sr-01 resin features a proprietary extractant covalently tethered to a silica support. The use of each resin is reported in the literature; Eichrom Sr Resin specifications, including the resin’s weight distribution ratio and capacity factor for analytes, have been reported but no such data have been published for IBC Analig® Sr-01 resin. In this work, batch studies were completed to determine the capacity and weight distribution ratio of both AnaLig® Sr-01 and Eichrom Sr resins for strontium and barium. This work shows that both resins retained Sr from aqueous samples, but Eichrom Sr resin provided superior Sr/Ba separation compared with Analig® Sr-01 resin.

**Introduction**

Strontium-90 has a relatively high cumulative fission yield (~6% for $^{235}\text{U} (n_{th},f)$) and is a pure beta ($\beta^-$) emitter. Radiometric analysis of $^{90}\text{Sr}$ present in an environmental sample requires that all other radioactive isotopes be removed from the sample to allow for accurate $\beta^-$ counting. The majority of the
radioisotopes present in samples originating from fission events are relatively easy to separate due to different chemistries, charges, and ionic radii. However, $^{140}$Ba has a similar cumulative yield as $^{90}$Sr and a half-life (~12 days), that is, (1) too long to wait for its complete decay, but (2) short enough to provide a non-negligible specific activity. $^5$ Barium and Sr exhibit the same oxidation states, very similar chemistries, and very similar ionic radii (1.4-1.6 and 1.2-1.4 Å, respectively $^6$), which explain the difficulties for separating Sr from Ba. Original methods relied on precipitation reactions or ion exchange to isolate Sr from Ba, but such methods were very pH sensitive and required a time-consuming process in which the procedure was repeated multiple times to obtain a satisfactory separation. $^7$

In the late 1980s and early 1990s, two new solid phase extraction (SPE) products were developed to separate Sr from environmental and spent fuel samples. IBC Advanced Technologies produces SPE resins that are based on prior work performed on cation-specific macrocycles such as crown ethers. $^8,^9$ These SPE resins utilize proprietary macrocyclic extractants attached to silica gel using a chain of carbons and oxygens. $^9-^{11}$ Published data show that the bonded macrocycle extractants’ log K values were within 10% of the reported values for the same unbound extractant in similar conditions. $^10$

In the early 1990s, a new extraction method used a solution of 1 M crown ether (4,4′(5′)-di-t-butylcyclohexano-18-crown-6) in 1-octanol that was sorbed onto an inert chromatographic resin (such as Amberchrom™ CG-71 or Amberlite™ XAD7). $^{12}$ This extraction technology is now commercially available as Sr resin from Eichrom Technologies. Important data have been reported on Sr separation using the Eichrom resin: the ligand structure, the expected equilibrium 2.1, and the uptake of specific metals on the resin. $^{12-^{16}}$

$$\text{Sr}^{2+}(\text{aq}) + \text{Crown}_{\text{org}} + 2\text{NO}_3^-(\text{aq}) \rightleftharpoons \text{Sr}($\text{Crown})(\text{NO}_3)_2(\text{org})$$  

2.1
With the characteristics of the Eichrom resin readily available, Eichrom Sr resin has achieved widespread use. The resin is a component of EPA and ASTM procedures for $^{90}$Sr measurements and is used in methods in radiation laboratories in the United States, the United Kingdom, and France.\textsuperscript{17-21}

Detailed properties of IBC Advanced Technologies AnaLig® Sr-01 are not readily available; a range for Sr binding capacity (0.1-0.3 mmol/g AnaLig®) is the only information provided by the manufacturer.\textsuperscript{22} IBC Advanced Technologies published literature data and acquired patents on separation methods using crown ethers. IBC Advanced Technologies also obtained patents on a covalent binding method to link organic molecules to silica for extraction, which may be the foundation for the Analig® Sr-01 resin.\textsuperscript{23-25} The available literature on AnaLig® Sr-01 resin reports $^{90}$Sr isolation from environmental samples: one study reports the recovery of $^{85}$Sr in the presence of Ba and other competitive ions using the AnaLig® resin, and additional studies show that the resin can effectively retain Sr.\textsuperscript{26-32} The literature lacks data on specifications of the AnaLig® Sr-01 resin to allow for the determination of an exact capacity or weight distribution ratio (the ratio of metal binding to the resin vs. the original load solution, D_w) for Sr. Studies have been conducted comparing the AnaLig® Sr-01 resin with the Eichrom Sr resin, but the only reported data were the radiochemical yields of $^{90}$Sr from environmental samples.\textsuperscript{33,34} It is evident that the AnaLig® Sr-01 resin can retain Sr from an environmental aqueous sample but there is a lack of data on how effective it is for the separation of Sr from the interfering Ba. The aim of this work is to provide key data for an effective comparison between AnaLig® Sr-01 and Eichrom Sr Resin for Sr/Ba separation.

**Experimental**

**Materials**

Reagent chemicals were obtained from Thermo Fisher Scientific, Waltham, MA, USA and JT Baker, Center Valley, PA, USA. Solutions were prepared using 18.2 M$\Omega$-cm distilled deionized water (DIW) from a Millipore Synergy Water Purification System (EMD Millipore, Billerica, MA, USA). Two lots of
AnaLig® Sr01 resin were acquired from IBC Advanced Technologies, Inc. (IBC Advanced Technologies, Inc., American Fork, UT, USA). The first lot of resin had a white color, while the second lot had a slight yellow color; the resin has a natural variation in color and both colors were within the manufacturer’s specifications. Eichrom Sr resin (100-150 μm) was obtained from Eichrom Technologies, LLC (Eichrom Technologies, Lisle, IL, USA).

Instrumentation
The samples were diluted in 2% HNO₃, and Sr and Ba concentrations were quantified using a Perkin Elmer Optima 3200 RL ICP-OES running WinLab32 for ICP, version 3.4 (Perkin Elmer, Waltham, MA, USA). The instrument was calibrated using dilutions of Inorganic Ventures Ba and Sr ICP certified standard solutions with concentrations from 0.1 to 50 ppm.

Methods
To confirm that the AnaLig® Sr-01 resin met manufacturer specifications, two brief gravity column studies were completed. Masses of 0.5 g of Sr-01 resin were loaded into gravity columns. DIW and 2 M HNO₃ were used as load solutions for the two studies. The column conditioning, sample loading, washes, and elution compositions for both experiments are listed in Table 1. The eluted solutions were collected and diluted with 2% HNO₃ for analysis via ICP-OES.
Table 2.1. The composition of each 5 mL fraction used in the gravity column quality check of AnaLig® Sr-01.

<table>
<thead>
<tr>
<th>Fraction</th>
<th>DIW Study</th>
<th>2 M HNO₃ Study</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.03 M EDTA (Wash)</td>
<td>0.03 M EDTA (Elution)</td>
</tr>
<tr>
<td>2</td>
<td>DIW (Condition)</td>
<td>2 M HNO₃ (Condition)</td>
</tr>
<tr>
<td>3</td>
<td>0.015 M Sr in DIW (Load)</td>
<td>0.015 M Sr in 2 M HNO₃ (Load)</td>
</tr>
<tr>
<td>4</td>
<td>DIW (Wash)</td>
<td>2 M HNO₃ (Wash)</td>
</tr>
<tr>
<td>5</td>
<td>0.03 M EDTA (Elution)</td>
<td>DIW (Wash)</td>
</tr>
<tr>
<td>6</td>
<td>0.03 M EDTA (Elution)</td>
<td>0.03 M EDTA (Elution)</td>
</tr>
<tr>
<td>7</td>
<td>0.03 M EDTA (Elution)</td>
<td>0.03 M EDTA (Elution)</td>
</tr>
<tr>
<td>8</td>
<td>-</td>
<td>0.03 M EDTA (Elution)</td>
</tr>
</tbody>
</table>

For batch studies, a mass of 0.04 g of AnaLig® Sr-01 was added to 3 mL of a 6.67 mM solution of Sr(NO₃)₂ in various concentrations of HNO₃ (ranging from 10⁻⁵ to 5 M) into 4 mL glass vials covered with poly-seal caps. The vials were equilibrated for 60 min using a rotary mixer. Upon equilibration, the vials were placed upright for 15 min to allow for the majority of the resin to settle out of solution. One milliliter of the supernatant was pipetted into an ultracentrifuge tube and centrifuged for 15 min at 3,000 rpm under a 1 mTorr vacuum with a Thermo Scientific Sorvall WX Ultra 80 Centrifuge, allowing for separation of particle of 150 nm or larger (Thermo Fisher Scientific, Waltham, Massachusetts, USA). A 0.5 mL aliquot of the supernatant was sampled for analysis. This procedure was repeated with a 6.67 mM Ba(NO₃)₂ solution in the same various HNO₃ concentration solutions and also using Eichrom Sr resin in place of the AnaLig® Sr-01, for Sr analyses. All samples were diluted with 2% HNO₃ before analyses with ICP-OES for metal concentration determinations. All experiments were run in triplicate and the errors are reported as 2σ of the replicate results.
Results and Discussion

Gravity Columns

As presented in Table 2.2, the AnaLig® Sr-01 columns were able to retain the majority of the Sr under both neutral (DIW) and acidic (2 M HNO₃) media. In both conditions, there was some early elution of Sr in the DIW wash that follows the initial loading. This was most likely due to overloading of the column; the manufacturer of AnaLig® Sr-01 resin reported a binding capacity of 0.1-0.3 mmol Sr/g resin²², however 0.15 mmol Sr/g resin was in the load solution of our work, which should not have exceeded the resin capacity. Another set of studies was performed in which the Sr concentration was kept below the manufacturer’s lower range of the binding capacity, and early Sr elution was significantly decreased. When used within the manufacturer capacity range, the column was able to effectively retain Sr, with the HNO₃ causing stronger retention, requiring the second EDTA elution to remove all of the Sr from the resin.

The combined recoveries of the two EDTA washes were 90% for both the DIW and 2 M HNO₃ column loads. This recovery is in agreement with multiple studies of the Analig® SR-01 resin.²⁷,²⁹,³⁰,³³

<table>
<thead>
<tr>
<th>Table 2.2. Percentage of total Sr recovered from the 5 mL 0.015 M Sr(NO₃)₂ load solution, using 0.5 g AnaLig® Sr-01 resin; A is DIW and B is 2 M HNO₃.</th>
</tr>
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<tbody>
<tr>
<td>% Sr Recovered</td>
</tr>
<tr>
<td>Fraction</td>
</tr>
<tr>
<td>Sr Load</td>
</tr>
<tr>
<td>HNO₃ Rinse</td>
</tr>
<tr>
<td>DIW Rinse</td>
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<tr>
<td>EDTA Strip</td>
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<td>EDTA Strip</td>
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<td>EDTA Strip</td>
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**Batch Studies**

The fraction of metal bound to the resin is defined by the concentration of the original load solution or weight distribution ratio \( (D_w) \) and can be calculated using the experimentally determined metal concentrations obtained before and after equilibration with the resins, as shown with the following equation:

\[
D_w = \left( \frac{A_0 - A_s}{w} \right) \left( \frac{V}{A_s} \right)
\]

where \( A_0 \) and \( A_s \) represent the concentrations (ppm) of the metal ion (Ba\(^{2+}\) or Sr\(^{2+}\)) in solution before and after contact with the resin, respectively; \( V \) is the volume (mL) of solution; and \( w \) is the mass (g) of the resin added to the vial.\(^{35} \) The metal ion binding capacities of the resins were calculated using the following equation:

\[
C = \frac{(A_0 - A_s) \cdot V \cdot 10^3 \text{ mmol/mol}}{10^6 \mu g / g \cdot MW \cdot w}
\]

where \( C \) is the capacity of the resin (millimole metal ion per gram of resin) and \( MW \) is the molecular weight of the metal ion of interest. Studies report capacities in milligrams of analyte per gram of resin, but the use of millimoles allows for direct comparisons between the resin capacities for Ba and Sr.

Resin batch studies using the IBC and Eichrom resins and solutions of Ba and Sr allowed for testing each resin capability for the separation of Sr from Ba. Figure 2.1 presents the weight distribution ratio, \( D_w \), across a wide range of HNO\(_3\) concentrations for Eichrom Sr (A) and AnaLig\(^{®}\) Sr-01 (B).
Figure 2.1. The weight distribution ratios ($D_w$) of Eichrom Sr Resin (A) and AnaLig® Sr-01 (B), across a range of nitric acid concentrations; reported errors are twice the standard deviation of three replicate samples for each concentration.

At 5 M HNO$_3$ concentrations, Sr $D_w$ is 77 using Eichrom Sr resin, while it is 43 for Ba; decreasing the acid concentration causes the weight distribution ratio of Sr to eventually reach zero; while at the HNO$_3$ concentrations at which Sr features a $D_w$ of 0, Ba $D_w$ ranges between 5 and 8. Strontium can be retained
and Ba rinsed off as long as the acid concentration is high enough; by lowering the acid concentration, the Sr can be eluted while some Ba is retained on the resin. The larger errors associated to some of the data reported in Fig. 1 are most likely due to static electricity rendering inconsistent weighing of Eichrom resin; these errors are propagated into the error seen in the reported capacities and weight distribution ratios. On the other hand, Sr and Ba are equally strongly retained by the AnaLig® Sr-01 resin for HNO₃ concentrations above 0.3 M, but both remained significantly sorbed on the resin at any acid concentrations down to 10⁻⁵ M, for which Sr Dₘ is 29 and Ba Dₘ is 53.

The capacities of the resins were determined from the same batch study. Eichrom Sr resin exhibits an increase in capacity as the concentration of nitric acid is increased. Maximum capacities for Sr and Ba were obtained in 5 M HNO₃ (0.22 and 0.18 mmol/g resin, respectively). At HNO₃ concentrations below 0.1 M, there is no retention of Sr, whereas the Ba capacity is approximately 0.05 mmol/g resin. Analig® Sr-01 exhibits a similar increase in capacities as HNO₃ concentration is increased: Sr capacities range from 0.15 mmol/g resin at 10⁻⁵ M HNO₃ to 0.30 mmol/g resin at 2 M HNO₃; Ba capacities are 0.22 and 0.27 mmol/g resin at 10⁻⁵ M and 2 M HNO₃, respectively. The retentions of Sr and Ba on the Analig® Sr-01 resin increases with an increased HNO₃ concentration from 0.01 to 0.1 M; the capacity increase is slightly more pronounced for Sr than for Ba. Due to the resin retaining Sr across the range of HNO₃ concentrations, a complexant (EDTA in this case) has to be used to strip Sr from the resin.

The weight distribution ratios of the Eichrom Sr resin best demonstrate how to separate Sr from Ba. High HNO₃ concentrations (e.g., 5 M) promote stronger Sr retention on the resin than Ba, indicating better Sr/Ba separation at such high HNO₃ concentrations. However, Sr is not retained on the resin in dilute acid, as shown by the distribution ratio and capacity, while some Ba is still retained on the resin. Therefore, Sr can be eluted from the resin (once Ba was separated with concentrated HNO₃) by rinsing the resin with a very dilute HNO₃ solution. Published procedures for Eichrom recommend loading the
sample onto the column in 8 M HNO₃ and rinsing with additional washes of 8 M HNO₃ to retain the Sr while removing the Ba. The batch studies presented in this article were only conducted up to 5 M HNO₃ concentrations because the 6.67 mM Ba(NO₃)₂ used in preparing the solutions is insoluble in HNO₃ at concentrations higher than 5 M. The Eichrom resin batch results presented in this article are in agreement with the results obtained with commonly accepted procedures for the Eichrom resin.¹⁵,¹⁸

The weight distribution ratio and resin capacities of the Analig® Sr-01 resin both increase as the concentration of acid is increased. This trend is similar to that of the Eichrom Sr resin and points to the Sr retention being dependent on HNO₃ concentrations. This dependency further reinforces the possibility that the ligand used is a crown ether. Nevertheless, a very long column or multiple separations would have to be utilized in order to separate Sr and Ba, as both metals are significantly retained on Analig® Sr-01 resin over a wide range of HNO₃ concentration. In order to compensate for this problem, the manufacturer recommended procedure is to strip the Sr from the resin using EDTA.²² However, the use of EDTA as a stripping rinse is not appropriate for samples containing multiple metal ions, because EDTA is a strong cation complexing agent but lacks selectivity capability. Any metals that remain on the resin following the washes will be stripped off along with the Sr in the EDTA rinses. AnaLig® Sr-01 would provide an effective means of concentrating Sr in environmental samples in which Ba is not a concern.

It is possible to isolate Sr from a mix of fission products without sample conditioning or purification step, but additional resins are typically used to remove non-alkali earth metals present in the samples and achieve best Sr separation yields.⁷,¹²,³⁶ Environmental samples that do not contain high levels of other fission products are typically purified using cation exchange.¹⁵,¹⁸ The removal of lanthanides can be obtained via Eichrom Ln resin or TRU resin.³⁷,³⁸ A number of ion-exchange resins are available for the removal of actinides from Sr samples: IBC Analig® Pu-02,²⁹ Eichrom TRU resin, Eichrom TEVA resin,
and Eichrom UTEVA resin.\textsuperscript{19,39} When using packed columns, the various extraction resins can be stacked on top of one another for the load solution to decrease the amount of time required for all of the separations. In the case of samples containing multiple fission products, additional extraction resins can be used prior to a Sr-specific resin to increase Sr yields. Still, environmental samples that do not contain interfering fission products would benefit from an ion-exchange column beforehand to pre-concentrate the aqueous Sr. In either situation, Analig\textsuperscript{®} Sr-01 and Eichrom Sr resin would benefit from the initial pre-processing steps.

**Conclusion**

Both IBC Advanced Technologies AnaLig\textsuperscript{®} Sr-01 and Eichrom Technologies Sr resin effectively retain Sr from aqueous solutions with similar maximum capacities and weight distribution ratios. The capacities and weight distribution ratios of the AnaLig\textsuperscript{®} Sr-01 were determined and compared with Sr resin under the same conditions. Both resins are capable of isolating and concentrating Sr from a simple aqueous solution, with similar capacities and distributions. However, the difference lies in that Eichrom has a more streamlined elution mechanism and more literature supporting various methods. As a result of this, no method development would be needed to use Eichrom’s resin to separate Sr from Ba in an environmental sample. While AnaLig\textsuperscript{®} Sr-01 exhibited similar Sr retention as Eichrom Sr resin, further method development would be required to determine a process through which the analytes (Sr or Ba) are eluted in a sequential fashion.

**Funding**

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References


29. Dulanská, S.; Antalík, I.; Labaška, M.; Remenec, B.; Mátel, A. Rapid determination of $^{239,240}$Pu, $^{238}$Pu, $^{241}$Am and $^{90}$Sr in high contaminated samples waste using combined SPE sorbents AnaLig® Pu-02, AnaLig® Sr-01 and DGA® Resin. J. Radioanal. Nucl. Chem. 2013, 295(3), 1635–1639.


Addendum

In order to better express the distribution ratios of the Eichrom and Analig® resins across the range of HNO₃ concentrations, a log-log plot was generated using the same data shown in Figure 2.1. This figure was not included in the published paper.

![Graph A](image)

![Graph B](image)

**Figure 2.2.** The log-log weight distribution ratios ($D_w$) of Eichrom Sr Resin (A) and Analig® Sr-01 (B), across a range of nitric acid concentrations; reported errors are twice the standard deviation of three replicate samples for each concentration.
CHAPTER 3
ANALYSIS OF ORGANIC AND HIGH DISSOLVED SALT SOLUTIONS WITH MINIMAL
SAMPLE PREPARATION USING INDUCTIVELY COUPLED PLASMA
OPTICAL EMISSION SPECTROMETRY

Preface
Solvent extraction studies are traditionally performed using radiotracers to analyze both the aqueous and organic phases via radiometric counting. The following studies sought to increase the utility of stable elements for solvent extraction studies. New methodology and instrumentation set-up was developed to allow for analyte quantifications in neutral solutions containing high salt concentrations and organic phases. The development of these techniques enables solvent extraction studies without the need for radiotracers for some elements, reducing cost and decreasing the long-term environmental impact of our studies.

This work was conducted in collaboration with a fellow graduate student in the Wall Research Group, Trevor Omoto. The lab work with the instrument and the writing of the paper was split equally, with myself taking the lead for the writing and editing of the paper. The following chapter has been submitted as a paper to the Journal of Analytical Atomic Spectroscopy.
Analysis of Organic and High Dissolved Salt Solutions with Minimal Sample Preparation Using Inductively Coupled Plasma Optical Emission Spectrometry

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Abstract

Quantification of analytes present in organic solvents or high salt content aqueous solutions using ICP-OES with minimal to no sample processing is desirable to decrease analyses turnaround time and sample cost. This work describes procedures used for Sr, V, and Y in 1-pentanol, 1-octane, 1-decanol, n-octane, and kerosene, substitute seawater, and NaCl solutions with concentrations as high as 5 molal using an ICP-OES with a standard nebulizer and spray chamber configuration. The detection limits of analyte in those extreme conditions decrease by less than a factor of ten compared to element quantification in dilute aqueous solution; however, the instrument maintained its normal precision and linearity in response. In dilute HNO₃, Sr, V, and Y feature LODs of $4 \times 10^{-2}$, 4, and 0.2 ng/L, respectively. A medium of 5 m NaCl shows LODs of 1, 4, and 4 ng/L for Sr, V, and Y, respectively. Organic analyses revealed the presence of a number of molecular emissions that occurred during the ionization of carbon; these emissions drastically increased backgrounds in the region around 400 nm. Dodecane solutions were found to require the addition of a metal complexant (Di-(2-ethylhexyl)phosphoric acid) to ensure the stability of the solutions. With the addition of the complexant to dodecane solutions, the LODs were 10, 5, and 4 ng/L for Sr, V, and Y, respectively.

Introduction

Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) is a common analytical tool, often available in academic and commercial settings. ICP-OES provides excellent trace element
quantifications with detection limits typically several orders of magnitude lower than those obtained with mass spectrometry, but with the added benefit of lower cost and greater instrument durability than mass spectrometry. However, the use of ICP-OES can be limited, as it is traditionally used for analyses of aqueous nature, prepared in a dilute mineral acid (typically in HNO₃ or HCl), and limited to several mass percent of dissolved solids. Solutions of high ionic strengths can be diluted for ICP-OES analysis, but this jeopardizes the quantification of trace elements. Hence, analyses of high salt solutions usually require a front-end sample preparation before analysis by ICP-OES. Typically, the sample is pre-concentrated and brought back up in dilute acid.¹⁻⁴ However, sample pre-concentration can be costly and increases processing time. ICP-OES elemental analysis of non-aqueous solutions is challenging, as methodologies demonstrate.⁵⁻⁶ Some of the organic sample analysis required the digestion of the organic solution or back-extraction to a dilute mineral acid.⁷⁻⁹ The majority of the techniques for the analysis without digestion or transposition to dilute aqueous acid were mostly developed by and for the petroleum industry.¹⁰⁻¹² Although the available literature is thorough and detailed for those sample types, even including an ASTM procedure,¹³ there is little procedure development for applications beyond the petroleum industry.

Fission product chemistries are often studied using radioanalytical techniques, but laboratory set-up for handling nuclear materials is uncommon, while the element chemistry remains unchanged whether the element is in its stable form or radioactive; the study of fission products in their stable form using ICP-OES allows for acquiring valuable data while avoiding handling nuclear materials. The elements Sr and Y are both high yield fission products and of importance for environmental monitoring and nuclear forensics; V has been considered as a chemical analog for the radioactive Tc, another high yield fission product of concern at contaminated sites (e.g. Hanford Site¹⁴), and nuclear forensics.¹⁵⁻²²
Understanding the chemistry of radioactive elements in high ionic strength aqueous solutions is important for nuclear waste management and environmental monitoring. Salt deposits can be used for nuclear waste repositories; for example, the Waste Isolation Pilot Plant is a U.S. repository for transuranic wastes and is situated within a 600 meter deep salt basin that was formed during the Permian Period.\(^{23}\) Additionally, fission products monitoring in seawater is also of great importance for nuclear forensics and environmental management.\(^{24}\)

Elemental quantification in organic phases by ICP-OES would allow for much development in the general scientific community. Literature and technical guides recommend a cooled spray chamber for volatile samples, but no specific values were apparent for what vapor pressure is too volatile for analysis using a traditional spray chamber.\(^{25}\) The propagation of molecular emissions is one of the unexpected difficulties encountered during elemental analysis in organic matrix. Brief mention of these emissions was found in technical guides but little detail was provided.\(^{26-28}\) While recent literature only makes brief mention of the molecular emissions, older literature reports the spectrum and the individual emission lines for C-C, C-N, and C-O molecular emissions.\(^{6,29}\) Molecular emissions are important to account for in organic matrix analysis because of the high carbon content of the solution compared to the analyte. Modifications of the instrument operating conditions can lessen the intensities of the interfering emissions, but some emissions appear to be unavoidable.\(^{10}\) An accurate knowledge of the individual emissions lines for these interferences and for the analytes of interest is crucial to avoid overlapping emission lines.\(^{6}\) While there is an abundance of literature in regards to analyses of organic solutions for applications in the petroleum industry, there is a lack of detailed work for general fields of study. The literature makes brief mention of the addition of stabilizing agents, but few details were found on its use in the organic phase. Acquisition of thermodynamic data for fission products is crucial for nuclear forensics and nuclear waste management. Such data can be determined using solvent extraction techniques, for which elements of choice are quantified in immiscible phases, one aqueous based and one organic non-aqueous phase.
Radioisotopes are traditionally used for such work and are quantified using radioanalytical techniques; elemental quantification in both phases using ICP-OES would allow for conducting solvent extraction experiments while avoiding the use of radioisotopes.\textsuperscript{21,30} Di-(2-ethylhexly)phosphoric acid (HDEHP) is commonly used as organic soluble complexing agent for the aforementioned solvent extractions and was chosen as proof of concept for this present work.\textsuperscript{30}

A number of accessories are available for some ICP-OES instruments that would further increase the possibilities of organic or high salt analyses including, but not limited to, desolvation devices (such as membrane desolvation and chilled spray chambers), sheathing devices, and flow injectors.\textsuperscript{31-33} In other cases, sample uptake rates were drastically decreased (0.08 mL/min), to allow for the analyses of organic solvents.\textsuperscript{34} In this study, we limited the ICP OES setup to one readily available in most laboratories and maintained traditional sampling rates.

This paper presents protocols for elemental quantification for Sr, Y, and V in aqueous solutions with high salt content and in non-aqueous solutions; this work was developed to support applications in nuclear forensics and environmental radiochemistry.

**Experimental**

**Reagents**

The following reagent grade chemicals were used without additional purification: concentrated HNO\textsubscript{3}, 1-pentanol, n-octane (Fisher Scientific, Waltham, MA); strontium, vanadium, and yttrium aqueous single element ICP-OES standards (each at 10,000 µg·mL\textsuperscript{-1}, Inorganic Ventures, Christiansburg, VA); strontium, vanadium, and yttrium single element petroleum standards (each at 5,000 µg·g\textsuperscript{-1}, VHG Labs, Manchester, NH); dodecane, mixture of isomers (Acros Organics, Thermo Fisher, Waltham, MA);
HDEHP (Alfa Aesar, Haverhill, MA); n-heptane (Mallinckrodt, St. Louis, MO); 1-octanol (Sigma Aldrich, St. Louis, MO); 1-decanol (Eastman Kodak, Rochester, NY).

**Instrumentation**

All ICP-OES analyses were performed using an Agilent 5100 SVDV ICP-OES with an SPS 3 autosampler with a 1.3 mm interior diameter inert PTFE sleeved probe, using a computer running ICP Expert Version 7.1.0.6821 (Agilent Technologies, Santa Clara, CA). For analyses of low salt concentration aqueous solutions, high salt aqueous solution, and organic solutions, separate instrument accessories were used to decrease the impact of salt and organic compounds on the instrument performance and reduce the risk of cross-contamination between solution types.

The following components were used for low salt content aqueous solutions: Agilent Easy Fit one-piece torch, 1.8 mm injector (Part #G8010-60288), Agilent Seaspray Nebulizer U-Series (Part #G8010-60255) (Agilent Technologies, Santa Clara, CA); Twister Spray Chamber with Helix (Part #20-809-9199HE), PVC peristaltic pump tubing (Glass Expansion, Pocasset, MA).

The following components were used for high salt content solutions: Easy Fit one piece torch, 1.8 mm injector (Part #G8010-60288) (Agilent Technologies, Santa Clara, CA); Seaspray S55074 Nebulizer, Twister Spray Chamber with Helix (Part #20-809-9199HE), Electra Argon Humidifier (Part #70-803-1266), PVC peristaltic pump tubing (Glass Expansion, Pocasset, MA).

The following components were used for organic solution analyses: VDV demountable torch for semi-volatiles, 1.4 mm injector (Part #G8010-60233) (Agilent Technologies, Santa Clara, CA); Conikal Nebulizer, 2 mL/min (Part # A31-07-UC2), Twister Spray Chamber with Helix (Part #20-809-9199HE), Viton and Solvaflx Peristaltic Pump Tubing (Glass Expansion, Pocasset, MA).


Instrument Operating Conditions

Table 3.1 lists the instrument operating conditions used for general sample analyses. In some cases, especially for the organic solutions, settings had to be further adjusted; the changes that were made are discussed in the Results and Discussion.

Table 3.1. Instrument operating conditions for each of the primary set-ups used in analyzing aqueous (2% HNO₃), high salt, and organic solutions.

<table>
<thead>
<tr>
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<th>Low salt aqueous solutions</th>
<th>High salt aqueous solutions</th>
<th>Organic solutions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow Rate (mL/min)</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Uptake Delay (s)</td>
<td>30</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>Rinse Time (s)</td>
<td>30</td>
<td>60</td>
<td>30</td>
</tr>
<tr>
<td>Integration Time (s)</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>RF Power (kW)</td>
<td>1.2</td>
<td>1.2</td>
<td>1.2</td>
</tr>
<tr>
<td>Stabilization Time (s)</td>
<td>15</td>
<td>9</td>
<td>15</td>
</tr>
<tr>
<td>Viewing Mode</td>
<td>SVDV*</td>
<td>SVDV*</td>
<td>SVDV*</td>
</tr>
<tr>
<td>Viewing Height (mm)</td>
<td>8</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>Nebulizer Flow (L/min)</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
</tr>
<tr>
<td>Plasma Flow (L/min)</td>
<td>12</td>
<td>12</td>
<td>12</td>
</tr>
<tr>
<td>Aux Flow (L/min)</td>
<td>0</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

*Synchronous Vertical Dual View

An argon humidifier was connected between the nebulizer gas supply and the nebulizer, for the high salt solutions. Increasing the humidity of the nebulizer gas is believed to prevent the salts from precipitating
and being deposited on the torch and spray chamber. Even with the argon humidifier, there was noticeable salt build up in the injector following analysis of 5 m NaCl solutions, probably due to insufficient rinsing at the completion of the run. The auxiliary flow gas was changed depending on the type of samples being analyzed; argon was used for high salt analyses, while a mixture of 80% argon and 20% oxygen was used for organic analysis, per the recommendation of the manufacturer.

The wavelengths at which the instrument was operated were selected based on their reported intensities in the ICP Expert software. The three elements selected for this work (Sr, Y, and V) feature wavelengths that are not overlapping. While the matrices presented some interfering wavelengths, the intensities of the analyte signals were orders of magnitude higher than the interferences and no procedure modification was necessary even when a cocktail of all three elements was used.

**Solutions**

A synthetic seawater was prepared according to ASTM procedure. The acidified seawater solution was prepared by adding concentrated HNO₃ to synthetic seawater to obtain a total HNO₃ concentration of 2%. A solution of 5 m NaCl was prepared using ACS grade NaCl (no Sr, V, or Y impurities were listed on the NaCl Certificate of Analysis) and 18 MΩ•cm deionized water. The 10 fold dilution of each of the two solutions was prepared using 18 MΩ•cm deionized water. Organic solutions consisted of the VHG petroleum single element standards diluted in dodecane with varying HDEHP concentrations (0 to 10⁻² M).

**Standard Solutions**

The low salt aqueous standard solutions (single element solutions of Sr, Y, or V; 10⁻⁵ – 10⁻⁷ M) were prepared via serial dilutions of the Inorganic Ventures aqueous standard solutions in 2% HNO₃. The high salt standard solutions (cocktail of Sr, Y, and V, 10⁻⁵ - 10⁻⁷ M) were prepared via serial dilutions of the
Inorganic ventures aqueous solutions in 5 m NaCl and ASTM substitute seawater. During the dilutions, an aliquot of HNO₃ was added to one set of seawater standards to bring the HNO₃ concentration to approximately 2%; accordingly, the concentration of the seawater for that set was approximately 98% of the concentration of the set that was not acidified. The substitute seawater has approximately 0.4 M NaCl and a total ionic strength of approximately 0.7 M, so it was included with the high salt solution analyses.

The organic standard solutions (single element solutions, Sr, V, or Y; 10⁻⁵ – 10⁻⁷ M) were prepared via gravimetric serial dilutions of single element VHG petroleum in dodecane; another set of organic standard solutions were prepared using the same method but the dodecane had an addition of HDEHP. Five sets of organic standard solutions for V and Y were prepared to quantify the influence of HDEHP concentration. Strontium was not included in this set of studies due to the weaker complexation of HDEHP with divalent metals and the strong molecular emissions that overlap many of the Sr emission lines. The organic standard solutions were prepared via serial dilution of the single element VHG petroleum standards into dodecane to obtain 10⁻², 10⁻⁴, 10⁻⁶, 10⁻⁸ or 0 M HDEHP for V and 10⁻², 10⁻⁴, 10⁻⁶, or 0 M HDEHP for Y. Petroleum standards of each V and Y were used; final concentration of V and Y was from 10⁻³ to 10⁻⁷ M. These samples were shaken vigorously and allowed to sit for 24 hours before ICP-OES measurement.

**Experimental**

Starting with the low salt content aqueous solutions, each set of prepared standards were measured using the ICP expert software with the instrumental conditions described previously. The instrument was then powered down, and the components were switched to the high salt hardware components so there would be no risk of cross contamination. After high salt solutions analyses, the system was powered down and switched over to the organic components. A CN molecular emission line was measured by defining a custom emission line (421.60 nm) in the OES software and then measuring the intensities when running different organic solvents. In the case of the more volatile standards, the analysis was stopped if any
inconsistencies were noticed in the plasma (i.e. flickering, sputtering, or drastic changes in intensity) to prevent damage to the torch. Using the various organic standards described above, the intensities were measured using a typical method to determine the limits of detections (LODs) and the effects of a complexant in the organic phase. Fitted background correction was applied to the measurements performed using the ICP Expert Software.

**Results and Discussion**

*Low salt content aqueous solutions*

The LODs were determined for each of the three elements of interest in 2% HNO₃ using the aqueous set-up. Detection limits were determined using a set of replicates with a concentration near LOD and a standard calibration curve, the LOD being determined using Equation 3.1.\(^{36}\)

\[
\text{LOD} = \frac{3\sigma}{m}
\]

Where \(\sigma\) is the standard deviation of 5 (or more) replicates near the LOD of that particular element and emission line and \(m\) is the slope for the plot of intensity as a function of analyte concentration at that emission line. The measured LODs are listed in Table 3.2. Sub-ppb LOD can be achieved with a working range from high ppt to low ppm levels without altering the instrument set-up. We decided that the wide working range was more desirable than simply going for as low of detection limits as possible. This allows a larger variety of samples to be analyzed without changing out parts or worrying about adjusting solution concentrations.
**Table 3.2.** Blank intensities and LOD of the three elements of interest in 2% HNO₃ using the aqueous setup; literature values for LODs and associated emissions wavelengths are listed for comparison.³⁷

<table>
<thead>
<tr>
<th></th>
<th>Sr</th>
<th>Sr</th>
<th>V</th>
<th>Y</th>
<th>Y</th>
<th>Y</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(407.771)</td>
<td>(421.552)</td>
<td>(322.28)</td>
<td>(324.228)</td>
<td>(361.104)</td>
<td>(371.029)</td>
</tr>
<tr>
<td>Blank Intensity</td>
<td>100</td>
<td>40</td>
<td>-200</td>
<td>6</td>
<td>30</td>
<td>8</td>
</tr>
<tr>
<td>LOD (ng/L)</td>
<td>20</td>
<td>3·10⁻²</td>
<td>4</td>
<td>0.6</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Reported LOD (ng/L)³⁷</td>
<td>4·10⁻²</td>
<td>8</td>
<td>4·10⁻²</td>
<td>(421.552 nm)</td>
<td>(290.882 nm)</td>
<td>(360.073 nm)</td>
</tr>
</tbody>
</table>

**High Salt solutions**

The quantification of LOD using Equation 3.1 is appropriate for dilute HNO₃ aqueous solutions, but it did not provide reliable values for the high salt solutions. In the case of Sr, the slopes of the high salt and dilute HNO₃ calibration curves were of relatively similar magnitudes, as were the standard deviations of the dilute sample replicates. However, the high salt solutions had significantly higher background levels. In some cases, using Equation 3.1 for high salt content solutions resulted in a calculated LOD with a lower theoretical intensity (calculated using the LOD concentration and the slope and intercept of the calibration curve) than the average background intensity. Clearly this would not be a viable detection limit and the detection limits were determined using Equation 3.2 for all of the high salt solutions and the dilute HNO₃ solution runs on the high salt setup for comparison; the background intensity is determined using the average of 5 replicates, σ is the standard deviation of those replicates, and m is the slope for the plot of intensity as a function of analyte concentration at that emission line.

\[
LOD = \frac{\text{Background intensity} + 3\cdot\sigma}{m}
\]

Table 3.3 presents the resulting LODs and intensities of the blanks. In the cases of Sr in undiluted seawater samples, the intensities overwhelmed the detector and no signals were measurable (except for the 421.552 nm emission for the acidified seawater blanks). This is most likely due to Ca and Sr being
present in the ASTM synthetic seawater; the concentration of Ca in the seawater was $1 \cdot 10^{-2}$ M and Sr was $2 \cdot 10^{-4}$ M. The sub-millimolar Sr concentration probably was not responsible for the signal overwhelming the detector but Ca features emission lines at 407.865 and 422.673 nm. The emission lines are typically far enough apart from the Sr lines to not be an issue, but the emissions peaks are probably much broader and the resolution in that region suffers when the Ca concentration is approaching molar levels. This theory is reinforced by the fact that the 10x dilution of seawater background emission for Sr at 421.552 nm is approximately 10 times smaller than that of the acidified seawater ($3.43 \cdot 10^6$ versus $2.25 \cdot 10^7$). In this case, further dilutions would avoid these problems, but as the intensity of the background is diluted, the analyte of interest will also be diluted. Choosing another analyte or emission wavelength that does not overlap with the background would be the simplest method; the difference in backgrounds intensities between 2% HNO$_3$ and the synthetic seawater was approximately one order of magnitude, for both V and Y. In those cases, a 10x dilution would have a less beneficial outcome since the analyte signal is being decreased by a factor of 10 when the background is already close to “normal” aqueous background levels.

The LODs for the 2% HNO$_3$ and 5 m NaCl solutions (Table 3.3) are approximately an order of magnitude higher than those in 2% HNO$_3$ on the traditional aqueous set-up (Table 3.2). The high salt set up still providing acceptable LODs; we decided not to investigate this further. Potential causes for decreased LOD could be from the differences in the instrument setup (the argon humidifier and nebulizer), the different method for calculating LODs, or simply that the high salt setup had undergone more wear and was no longer operating at its peak potential due to exposure to everything up to 5 m NaCl. In all likelihood, the difference in LODs was due to combination of all three factors.
Table 3.3. Blank intensities and limits of detection (LOD) (3σ) with blank solutions using the high salt set-up.

<table>
<thead>
<tr>
<th></th>
<th>Sr (407.771)</th>
<th>Sr (421.552)</th>
<th>V (311.070)</th>
<th>V (311.837)</th>
<th>Y (361.104)</th>
<th>Y (371.029)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>2% HNO₃</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Blank Intensity</td>
<td>200</td>
<td>40</td>
<td>9</td>
<td>7</td>
<td>50</td>
<td>10</td>
</tr>
<tr>
<td>LOD (ng/L)</td>
<td>0.2</td>
<td>0.3</td>
<td>5</td>
<td>1</td>
<td>0.3</td>
<td>0.5</td>
</tr>
<tr>
<td><strong>10x dil. Seawater</strong></td>
<td>7·10⁶</td>
<td>3·10⁶</td>
<td>20</td>
<td>-7</td>
<td>40</td>
<td>70</td>
</tr>
<tr>
<td>Blank Intensity</td>
<td>400</td>
<td>200</td>
<td>4</td>
<td>1</td>
<td>0.4</td>
<td>0.3</td>
</tr>
<tr>
<td><strong>Acidified Seawater</strong></td>
<td>*</td>
<td>2·10⁷</td>
<td>-200</td>
<td>1</td>
<td>70</td>
<td>100</td>
</tr>
<tr>
<td>Blank Intensity</td>
<td>*</td>
<td>2·10⁷</td>
<td>-200</td>
<td>1</td>
<td>70</td>
<td>100</td>
</tr>
<tr>
<td>LOD (ng/L)</td>
<td>*</td>
<td>**</td>
<td>5</td>
<td>1</td>
<td>1</td>
<td>0.9</td>
</tr>
<tr>
<td><strong>Seawater</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Blank Intensity</td>
<td>*</td>
<td>*</td>
<td>20</td>
<td>20</td>
<td>80</td>
<td>100</td>
</tr>
<tr>
<td>LOD (ng/L)</td>
<td>*</td>
<td>*</td>
<td>7</td>
<td>1</td>
<td>2²</td>
<td>2</td>
</tr>
<tr>
<td><strong>0.5 m NaCl</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Blank Intensity</td>
<td>4·10³</td>
<td>2·10³</td>
<td>10</td>
<td>10</td>
<td>40</td>
<td>30</td>
</tr>
<tr>
<td>LOD (ng/L)</td>
<td>0.5</td>
<td>0.5</td>
<td>4</td>
<td>2</td>
<td>2</td>
<td>0.7</td>
</tr>
<tr>
<td><strong>5 m NaCl</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Blank Intensity</td>
<td>2·10⁴</td>
<td>9·10³</td>
<td>10</td>
<td>20</td>
<td>6</td>
<td>20</td>
</tr>
<tr>
<td>LOD (ng/L)</td>
<td>2</td>
<td>1</td>
<td>6</td>
<td>4</td>
<td>4</td>
<td>5</td>
</tr>
</tbody>
</table>

*The intensity overwhelmed the detector
* *The intensity of the background overwhelmed any signal of the strontium in the calibration solutions
Although there was a decrease in sensitivity when switching the instrument over to the high salt configuration, the decrease in sensitivity for 10x dilutions of the seawater and NaCl solutions were minimal. As mentioned earlier, Sr is the exception due to background interferences. In the cases of both lines for V and Y, there was essentially no difference in detection limits for both the 10x dilutions of seawater and 0.5 m NaCl. It appears that these two solutions can be analyzed without having to worry about instrument wear and poor LODs; there was minimal salt build-up on the instrument after several hours of aspirating the solutions. Both the 0.5 m NaCl and the 10x dilution of seawater caused a noticeable change in the plasma color, from the typical blueish-white color to an orange, but it only lasted as long as the sample was being analyzed. As soon as the rinse solution made it to the torch, the plasma went back to the normal blueish-white color.

The nearby Na II lines at 405.967, 408.1369, 421.627 and 423.096 nm and Na I lines at 405.66, 421.309, 421.613, and 422.076 nm combined with the molal concentrations of Na led to increased background levels for the 407.771 and 421.552 nm Sr lines. Even though the Sr backgrounds are increased by more than an order of magnitude for 0.5 m NaCl and 2 orders of magnitude for 5 m NaCl, linear calibration curves were still achievable. The LODs for both Sr lines increased by approximately an order of magnitude for both 0.5 m and 5 m NaCl solutions.

There seems to be no major issues with analyzing solutions similar to the 0.5 m NaCl and 10x dilution of seawater. The salt concentration does not seem to have substantial negative effect on the instrument’s performance or analyte emissions. However, the two Sr emission lines show how crucial it is to take into account any potential elements that will be present in the background solution.

For the undiluted synthetic seawater and the acidified synthetic seawater, V and Y showed some variation in background levels; in the case of V the background intensities decreased, while Y saw an increase in
background levels. The decrease in background intensity for V could be due to the concentration of the salts starting to overwhelm the energy of the plasma and causing there to be less available energy for the ionization of the analytes. In terms of LODs, both V and Y had shifts of approximately a factor of two. For both V and Y, it would be more effective in terms of LODs to measure the undiluted seawater samples instead of diluting it prior to analysis. The acidification seemed to have minimal effect on both background intensities and LODs, but it would probably be beneficial for the increased stability of samples.

The 5 m NaCl was the most concentrated solution analyzed in this work and linear calibration plots were still obtainable. For the emissions lines for all 3 elements, the LODs decreased by up to a factor of 10 when compared with the dilute HNO₃ LODs in the same setup. In the case of the Sr lines, this was due partly to the increase in background levels discussed earlier, but for all of the elements this was at least partially due to the fact that the 5 m NaCl was simply consuming more of the available energy of the plasma. This theory was reinforced when, after completion of the run, the torch was removed and the torch chamber was opened. The torch itself had a coating of NaCl on the outer tube and there was the beginning of NaCl build-up in the injector. The torch chamber had noticeable amounts of NaCl coverage and NaCl completely coated the cone above the torch. While clean-up was easy, 5 m NaCl appears to be beyond the reasonable limits for routine sample analysis. For a one-off sample or a sample where LODs and speed are equally important, it is possible to get quantitative results in salt concentrations up to 5 m. When compared with the 0.5 m NaCl solutions, the 5 m did not show a 10x decrease in LOD. Therefore, for an urgent sample where the LOD is critical, analyzing the concentrated salt solution will provide better overall detection than diluting the sample. 0.5 m NaCl provides better LODs and backgrounds than 5 m, but when the high salt solution is diluted by a factor of 10, so is the analyte; hence, while the LOD is improved, it is not a significant enough improvement to justify diluting the analyte by a factor of ten.
We did not attempt to optimize the high salt set-up. Only the 5 m NaCl solution seemed to lead to salt build-up on the torch and in the chamber. One set of samples were analyzed without the auxiliary gas flow and there was drastically more salt build up on the torch. While the auxiliary gas flow does not prevent salt from being deposited on the chamber, it is very effective at preventing build-up on the torch. Without the auxiliary flow, there was eventually complete blockage of the injector from the salt build-up. This could be further prevented by choosing a torch with a wider injector or adjusting the nebulizer flow. We did not investigate the effectiveness of the argon humidifier because we did not observe any salt build-up before the injector. By optimizing the nebulizer and torch selection and nebulizer gas flow, one may be able to further optimize the high salt setup and prevent salt build up on the injector.

_Molecular Emission lines from Organic Solvents_

Organic solutions analyses via ICP-OES present the additional challenge of dealing with interferences from C-C and C-N molecular emissions produced by the incomplete ionization of the organic solvent when introduced into the plasma. These emissions can cover broad portions of the recorded spectrum and have high intensities, creating a high background signal over a wide range of wavelengths, and making analysis of some metal emission lines difficult or impossible.

Six different organic solvents listed in Table 3.4 were analyzed under identical conditions as described in Table 3.1 to determine the magnitude of the 421.6 nm C-N molecular emission of each solvent. These solvents were selected based on the differences in length of their carbon backbones to determine what impact hydrocarbon complexity had on the effective ionization of organic solvents by ICP in regards to molecular emission.
Table 3.4. The reported densities, boiling points, and vapor pressures (at 25°C and 1 atm) of the solvents used when examining the CN molecular emission line (421.6 nm).

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Density (g·cm⁻³)</th>
<th>Boiling Point (°C)</th>
<th>Vapor Pressure (kPa)</th>
<th>Intensity at 421.6 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Pentanol³⁹</td>
<td>0.8144</td>
<td>137.6</td>
<td>0.259</td>
<td>34720.29</td>
</tr>
<tr>
<td>1-Octanol³⁹</td>
<td>0.8262</td>
<td>194.7</td>
<td>0.01</td>
<td>34776.53</td>
</tr>
<tr>
<td>1-Decanol³⁹</td>
<td>0.8294</td>
<td>229</td>
<td>0.009</td>
<td>33405.82</td>
</tr>
<tr>
<td>n-Octane³⁹</td>
<td>0.7022</td>
<td>125.62</td>
<td>1.86</td>
<td>193598.9</td>
</tr>
<tr>
<td>Dodecane³⁹,⁴⁰</td>
<td>0.75</td>
<td>175-192</td>
<td>0.0016*</td>
<td>70263.16</td>
</tr>
<tr>
<td>Kerosene⁴¹</td>
<td>0.8</td>
<td>175-195</td>
<td>0.07</td>
<td>57964.19</td>
</tr>
<tr>
<td>Water</td>
<td></td>
<td></td>
<td></td>
<td>82.33</td>
</tr>
</tbody>
</table>

*No vapor pressure literature data was available for mixture of isomers dodecane that was used, this value is for n-dodecane

Table 3.4 lists the physical properties of each of the six solvents analyzed in this experiment and their emission intensities at 421.6 nm. The three alcohols measured have C-N emission intensities within error of each other, despite varying in hydrocarbon chain length by up to five carbons. Of the two alkanes measured, octane had the higher emission peak, approximately 2.8 times that of the emission peak observed for dodecane, while kerosene, a mixture of hydrocarbons varying from 6 to 16 carbons, had an emission intensity somewhere between that of dodecane and the three measured alcohols.

The identical peak emissions between the three alcohols suggest that there is no correlation between a solvent hydrocarbon length and its intensity at the 421.6 nm molecular emission line. The largest observed emission of the six analyzed organic solvents was that of the 8 carbon long octane, which had a peak area that was 5 times greater than that of the similarly 8 carbon long solvent octanol. The
differences between these two 8 carbon solvents reinforce the idea that the molecular emission lines are not impacted by carbon chain length.

The variation in molecular emissions intensity during organic solvent analysis on ICP-OES is due primarily to solvent volatility. Higher volatility solvents such as short chained alkanes and alcohols turn to gas more readily during nebulization and thus a greater volume of solvent is sent into the ICP torch. This higher volume of solvent entering the plasma would cause quenching in the plasma and decrease ionization efficiency, leading to an increased creation of molecular emissions from incompletely ionized hydrocarbons. The literature reports similar observations regarding the volatility of a sample affecting the plasma stability.29,33,34,42-44

We found that without a chilled spray chamber, the volatility of the solvent was the major limiting factor, defining which samples we could analyze. For alkanes, we were able to successfully analyze n-octane solutions despite the increased vapor pressure compared to our traditional organic analysis using dodecane or kerosene. However, too much quenching occurred with heptane (6.09 kPa vapor pressure39). For alcohols, we were able to analyze 1-pentanol without any issues but switching to isopropanol (2.76 kPa vapor pressure39) led to quenching of the plasma. A chilled spray chamber would allow for analyzing additional organic solvents but it is by no means necessary for organic solvent analyses if one chooses the appropriate solvent(s).

**Effect of Organic Standard Composition**

Commercially available oil standards for metal analysis are typically prepared with an undisclosed stabilizer added to maintain metal analyte dispersion in organic solvents. In the process of preparing calibration standards with high dilution factors (up to a factor of 1,000,000), we found necessary to add a specific reagent to maintain metal dispersion in organic solvents. Figure 3.1 and Figure 3.2 show the
results of added HDEHP in dodecane on the V and Y signal intensity at six different concentrations of dissolved metals. The signals were normalized to the intensity at 0.01 M HDEHP.

At 100 ppm V, the signal intensity for the standard solution prepared without any HDEHP complexant is 91% of the intensity of the signal produced by the 100 ppm standard in 0.01 M HDEHP. For V standards at the lowest concentration tested, 10 ppb, the signal intensity for the V standard produced in dodecane without any HDEHP complexant is only 20 percent of the intensity of the 10 ppb standard produced in 0.01 M HDEHP. The addition of 0.01 M HDEHP in dodecane had a 5x increase in the signal intensity of standards near the limit of quantification.

**Figure 3.1.** 311.07 nm emission line intensity for varied V concentrations in increasing HDEHP concentrations; the signal was normalized to the intensity of the $10^{-2}$ M HDEHP in dodecane samples.
Figure 3.2. 324.228 nm emission line intensity for varied Y concentrations in increasing HDEHP concentrations; the signal was normalized to the intensity of the $10^{-2}$ M HDEHP in dodecane samples.

The Y standards show a similar trend. While there is no noticeable difference observed in the signal intensity of 100 ppm Y standards prepared at any concentration of HDEHP in dodecane, as the concentration of Y in the prepared standards decreases, the differences between the 0.01 M standards and the standards containing lower concentrations of HDEHP becomes more pronounced. At 10 ppb Y, the standard prepared in 0 M HDEHP has a signal that is approximately 40 percent as intense as the 10 ppb Y standard prepared in 0.01 M HDEHP.
Two trends were observed in these experiments. Firstly, increasing the organic soluble complexant of serial dilution calibration standards to 0.01 M increases the observed signal intensity when measuring metals in dodecane on ICP-OES. Secondly, the effect of adding an organic soluble complexant on signal intensity is more pronounced at higher dilution factors, than at lower dilution factors. That is to say that the benefit of adding an organic complexant to prepared calibration standards appears to be highest at lower concentrations of metals.

An organic soluble ligand, such as HDEHP, is used to maintain the solubility of a positively charged metal ion in a non-polar organic solvent, such as dodecane. These ligands complex with the metal ion via negatively charged functional groups (phosphate in the case of HDEHP) and create a metal ligand complex with zero net charge that is soluble in an organic non-polar medium. The proposed mechanism for the loss of metal ions in higher dilutions of the vanadium and yttrium oil standard is the corresponding dilution of the proprietary Conostan stabilizer included in the oil standard itself. Conostan oil standards employ an unidentified and proprietary “stabilizer” to maintain the solubility of the metal ions in oil. With lower dilution factors of this oil standard in dodecane, the concentration of the stabilizer is still in sufficient concentration to maintain solubility of the metal ion in the organic solvent. As this dilution factor increases, the stabilizer is no longer in sufficient concentration to maintain metal ion solubility. The addition of the organic soluble ligand HDEHP is believed to counter this loss in solubility by binding with the metal ions and creating organic soluble complexes. Other studies reported losses of analyte in the organic phase and it is the author’s opinion that the losses were also due to solubility issues with the metal in the organic solvent.
Organic Calibration curves

The relative signal intensities produced by the standards described above allowed for determining LOD and LOQ for V and Y in organic solutions. Table 3.5 presents the calibration and LOD results for Sr, Y, and V, in aqueous and organic solutions; all LOD values presented in Table 3.5 were calculated using Equation 3.2. We observed an approximate 40 percent decrease in the sensitivity for vanadium and yttrium in dodecane analyses when compared to the standard analysis of these metals in 2% HNO₃. There is also a corresponding increase in the LOD for these metals in dodecane when compared to 2% HNO₃. The difference in LOD between aqueous and organic solvents is markedly different for the three metals. The LOD for the 311.07 nm emission line for V worsened by a factor 1.4 in dodecane, the 324.228 nm signal of yttrium worsens by a factor of 6.5, and due to the overlap with the molecular emissions region, the 421.552 nm signal for Sr decreased by 3 orders of magnitude.

Table 3.5. Calibration curve results and LODs for Sr, Y, and V in aqueous and organic solutions.

<table>
<thead>
<tr>
<th></th>
<th>Sr (421.552 nm)</th>
<th>V (311.07 nm)</th>
<th>Y (324.228 nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Aqueous solution (2% HNO₃)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Blank Intensity</td>
<td>40</td>
<td>-200</td>
<td>6</td>
</tr>
<tr>
<td>Slope</td>
<td>2·10¹¹</td>
<td>4·10⁹</td>
<td>1·10¹⁰</td>
</tr>
<tr>
<td>Intercept</td>
<td>2·10³</td>
<td>-300</td>
<td>9</td>
</tr>
<tr>
<td>LOD (ng/L)</td>
<td>3·10⁻²</td>
<td>4</td>
<td>0.6</td>
</tr>
<tr>
<td><strong>Organic (Dodecane)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Blank Intensity</td>
<td>3·10⁴</td>
<td>90</td>
<td>100</td>
</tr>
<tr>
<td>Slope</td>
<td>2·10¹¹</td>
<td>3·10⁹</td>
<td>8·10⁹</td>
</tr>
<tr>
<td>Intercept</td>
<td>6·10³</td>
<td>20</td>
<td>-50</td>
</tr>
<tr>
<td>LOD (ng/L)</td>
<td>10</td>
<td>5</td>
<td>4</td>
</tr>
</tbody>
</table>
These results demonstrate we can achieve a similar sensitivity and detection limit in organic solvents, within an order of magnitude, as can be achieved in an ideal solvent such as 2% HNO₃. The largest limiting factor in organic analysis is the standard deviation between replicate measurements, which trends higher in organic solutions when compared to HNO₃. Sample introduction is proposed as the most likely cause for the higher standard deviation and LOD in organic sample measurement. Uneven nebulization in the spray chamber was apparent during organic sample introduction; however these symptoms could be diminished by fine tuning the peristaltic pump pressure and rotational speeds, or by increasing instrument read time to smooth signal variation due to uneven sampling.

**Conclusions**

Element quantification in organic solutions and aqueous solutions containing high salts can be efficiently achieved using ICP-OES with minor modifications to the instrument setup. A simple change of the consumable components allowed for the analysis of a large range of complex solutions. A carbon buildup during organic analysis and the salt buildup during high salt containing solution analysis can both be prevented with the addition of an auxiliary gas. Several organic solvents can be analyzed without the addition of a chilled spray chamber, by simply adjusting sample flow rates and tubing selection.

Even with the changes made to the instrument and the increased complexity of the solutions to analyze, sample detection limits typically only increase by a factor of 10. With this almost negligible change in detection limits, the option to analyze a large variety of solution types is readily available to ICP-OES users without requiring significant investments.
Acknowledgements

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CHAPTER 4
A NEW BATEMAN DERIVED TECHNIQUE FOR THE SIMULTANEOUS DETERMINATION OF STRONTIUM-90 AND YTTRIUM-90

Introduction

Strontium-90 has a cumulative fission yield of approximately 6% and accordingly its daughter, $^{90}$Y, has a similar yield.\(^1\) The high yield and the longer half-life of $^{90}$Sr (28.8 years) means that it can provide valuable information for nuclear forensics.\(^2\) Ingested $^{90}$Sr can replace Ca in bone and teeth, due to the chemical similarities between Sr and Ca. Accordingly, $^{90}$Sr is an important isotope for environmental monitoring.\(^8\)\(^-\)\(^12\)

Strontium-90 is a pure $\beta^-$ emitter and $^{90}$Y has a gamma emission, with a branching ratio of $1.4 \cdot 10^{-6}\%$ making it also essentially a $\beta^-$ emitter. Due to the lack of gamma or alpha emissions, $^{90}$Sr and $^{90}$Y are typically quantified via liquid scintillation counting (LSC). Due to the wide energy distribution of $\beta^-$ decay and the lack of resolving power with LSC, $^{90}$Sr and $^{90}$Y cannot be individually resolved when both are present in an LSC sample. There are several techniques available to compensate for this. Chemical separations, such as precipitation, solid phase extraction, or liquid-liquid extraction, are one of the most prevalent methods. With these techniques, the Sr and Y are separated and then counted; $^{90}$Y ingrowth can also be measured in the $^{90}$Sr sample following separation.\(^13\)\(^-\)\(^22\) The second primary technique is relying on the higher energy $\beta^-$ decay of $^{90}$Y and resolving its activity using Cherenkov counting. The energy of the $\beta^-$ decay of $^{90}$Sr is too low to cause significant Cherenkov emissions, so the signal measured is only from $^{90}$Y. Once $^{90}$Y activity is known, LSC can be used to determine the total activity and then subtract the $^{90}$Y activity to obtain $^{90}$Sr activity.\(^23\)\(^-\)\(^28\)
This present study demonstrates the quantification of the activities of both $^{90}\text{Sr}$ and $^{90}\text{Y}$ in a sample without sample treatment or lengthy wait, taking advantage of secular equilibrium properties of the two radioisotopes and using the Bateman Equation.$^{29}$

**Experimental**

*Instrumentation*

Stable isotopes of Sr and Y were quantified via ICP-OES using an Agilent 5100 SVDV ICP-OES, equipped with an SPS 3 autosampler with a 1.3 mm interior diameter inert PTFE sleeved probe, using a computer running ICP Expert Version 7.1.0.6821 (Agilent Technologies, Santa Clara, CA). The exact instrument set-up conditions for aqueous and organic sample analyses are detailed in Table C.1. Samples were diluted prior to analysis with 2% HNO$_3$ or $10^{-2}$ M HDEHP in dodecane for aqueous and organic solutions, respectively.

Radioactive isotopes of Sr and Y were quantified with a Beckman LS 6500 scintillation counter (Beckman Coulter, Brea, CA) using Ecoscint Original scintillating cocktail (National Diagnostic, Atlanta, GA). The counting window was set for all channels to be open and count times were 5 or 20 minutes, dependent on the activity of the sample. In order to maintain satisfactory counting efficiencies, the final samples were counted in 20 mL vials with 19 mL of Ecoscint scintillation fluid. A larger volume of scintillation fluid was used in order to ensure the high energy $^{90}\text{Y} \beta^-$ would have a decreased probability of escaping without interacting with the scintillator. With this geometry, efficiencies for both $^{90}\text{Sr}$ and $^{90}\text{Y}$ are approximately 99%.$^{30}$
Table 4.1. Instrumental operating conditions for the ICP-OES used in the analysis of stable aqueous and organic samples.

<table>
<thead>
<tr>
<th></th>
<th>Aqueous Solutions</th>
<th>Organic Solutions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Torch</td>
<td>Torch: 1.8 mm injector, one piece Torch Agilent G8010-60228</td>
<td>Torch: 1.4 mm injector, demountable Torch Agilent G8010-60233</td>
</tr>
<tr>
<td>Spray Chamber</td>
<td>Twister Spray Chamber with helix, Glass Expansion 20-809-9199HE</td>
<td>Glass Expansion</td>
</tr>
<tr>
<td>Nebulizer</td>
<td>SeaSpray 2mL/min Glass Expansion A14-07-USS2</td>
<td>Conikal 2mL/min Glass Expansion A14-07-UC2</td>
</tr>
<tr>
<td>Pump Tubing Material</td>
<td>PVC</td>
<td>Solva Flex</td>
</tr>
<tr>
<td>Sample Pump Speed (rpm)</td>
<td>12</td>
<td>12</td>
</tr>
<tr>
<td>Uptake Delay (s)</td>
<td>25</td>
<td>30</td>
</tr>
<tr>
<td>Rinse Time (s)</td>
<td>30</td>
<td>40</td>
</tr>
<tr>
<td>Read Time (s)</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>RF Power (kW)</td>
<td>1.20</td>
<td>1.20</td>
</tr>
<tr>
<td>Stabilization Time (s)</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>Viewing Mode</td>
<td>SVDV*</td>
<td>SVDV*</td>
</tr>
<tr>
<td>Viewing Height (mm)</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>Nebulizer Flow (L/min)</td>
<td>0.7</td>
<td>0.7</td>
</tr>
<tr>
<td>Plasma Flow (L/min)</td>
<td>13</td>
<td>12</td>
</tr>
<tr>
<td>Aux Flow (L/min)</td>
<td>0</td>
<td>1</td>
</tr>
</tbody>
</table>

*SVDV: Synchronous Vertical Dual View
Reagents

Reagent grade chemicals were obtained from Sigma Aldrich (St. Louis, MO), JT Baker (Center Valley, PA), Thermo Fisher (Waltham, MA), and Alfa Aesar (Ward Hill, MA). Single element aqueous phase ICP standards were purchased from Inorganic Ventures (Christiansburg, VA) and prepared as multi-element cocktails in 2% HNO₃ via gravimetric serial dilutions. Single element organic phase ICP standards were purchased from VHG Labs (Manchester, NH) and prepared as multi-element cocktails via gravimetric serial dilution in 10⁻² M di-(2-ethylhexyl)phosphoric acid (HDEHP) in dodecane. Strontium-90 radiotracer was purchased through the National Isotope Development Center (Oak Ridge, TN) and was received from Pacific Northwest National Laboratory (Richland, WA). Thenoyltrifluoroacetone (TTA) and 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (HEHEHP) were purified prior to use, the purifications are detailed in Appendix B, all other reagents were used without purification.

Bateman Derived Counting Technique

The isotopes ⁹⁰Sr and ⁹⁰Y are both β⁻ emitters (⁹⁰Y has a gamma emission, but its branching ratio of 1.4·10⁻⁶% makes gamma spectroscopy inadequate for lower activity levels) and a method was developed to simultaneously determine each isotopes' activity via successive counting on LSC over a period of time (without any separations) and relying on the secular equilibrium behavior of the ⁹⁰Sr/⁹⁰Y system. Secular equilibrium applies to a system in which the parent has a much larger half-life than the daughter and is a state achieved when parent and daughter isotopes have reach equal activities. The difference in decay rate constants is expressed by the criteria shown in Equation 4.1.³¹

\[
\frac{\lambda_{\text{parent}}}{\lambda_{\text{daughter}}} \leq 10^{-4}
\]

Strontium-90 has a half-life of 28.8 years and ⁹⁰Y has a half-life of 2.67 days; accordingly their respective decay rate constants are 6.60·10⁻⁵ d⁻¹ and 0.260 d⁻¹. The decay rate constant ratio, between parent and daughter is 2.54·10⁻⁴, within the definition of secular equilibrium. With the assumption that the sample is
isotopically pure, (i.e. it is composed of only $^{90}$Sr and $^{90}$Y) the total activities can be calculated according to Equations 4.2 and 4.3.

$$A_{tot}^0 = A_{Sr}^0 + A_Y^0$$  \hspace{1cm} 4.2

$$A_{tot} = A_{Sr} + A_Y$$  \hspace{1cm} 4.3

Using Equation 4.2, the initial ratio of $^{90}$Sr to total initial activity can be defined as Equation 4.4.

$$x = \frac{A_{Sr}^0}{A_{tot}^0}$$  \hspace{1cm} 4.4

This ratio can then be used to define the initial activities of $^{90}$Sr and $^{90}$Y in terms of the initial total activity (Equations 4.5 and 4.6).

$$A_{Sr}^0 = x \cdot A_{tot}^0$$  \hspace{1cm} 4.5

$$A_Y^0 = (1-x) \cdot A_{tot}^0$$  \hspace{1cm} 4.6

Using the exponential decay equation where $N$ is the number of atoms (4.7), the initial activity equations can be expressed in terms of the number of atoms ($N$) instead of radioactive decay (Equations 4.8 and 4.9).

$$A = \lambda \cdot N$$  \hspace{1cm} 4.7

$$N_{Sr}^0 = \frac{x \cdot A_{tot}^0}{\lambda_{Sr}}$$  \hspace{1cm} 4.8

$$N_Y^0 = \frac{(1-x) \cdot A_{tot}^0}{\lambda_Y}$$  \hspace{1cm} 4.9

The Bateman Equation accounts for the activities of a parent and daughter (in this case, the Sr and Y) as defined with Equations 4.10 and 4.11 respectively.\footnote{29,31}

$$N_{Sr} = N_{Sr}^0 \cdot e^{\lambda_{Sr} \cdot t}$$  \hspace{1cm} 4.10

$$N_Y = \frac{\lambda_{Sr}}{\lambda_Y - \lambda_{Sr}} \cdot N_{Sr}^0 \cdot \left( e^{\lambda_{Sr} \cdot t} - e^{\lambda_Y \cdot t} \right) + N_Y^0 \cdot e^{\lambda_Y \cdot t}$$  \hspace{1cm} 4.11
The initial quantities of Sr and Y are unknown and Equations 4.8 and 4.9 are substituted into Equations 4.10 and 4.11; the initial quantities are expressed in terms of initial total activity, which is measureable via LSC, leading to Equations 4.12 and 4.13. Equation 4.13 can be further simplified to 4.14.

\[
N_{Sr} = \left( \frac{x \cdot A^0_{tot}}{\lambda_{Sr}} \right) \cdot e^{\lambda_{Sr} \cdot t} \tag{4.12}
\]

\[
N_{Y} = \frac{\lambda_{Sr}}{\lambda_{Y} - \lambda_{Sr}} \cdot \left( \frac{x \cdot A^0_{tot}}{\lambda_{Sr}} \right) \cdot \left( e^{\lambda_{Sr} \cdot t} - e^{\lambda_{Y} \cdot t} \right) + \left( \frac{(1 - x) \cdot A^0_{tot}}{\lambda_{Y}} \right) \cdot e^{\lambda_{Y} \cdot t} \tag{4.13}
\]

\[
N_{Y} = \left( \frac{x \cdot A^0_{tot}}{\lambda_{Y} - \lambda_{Sr}} \right) \cdot \left( e^{\lambda_{Sr} \cdot t} - e^{\lambda_{Y} \cdot t} \right) + \left( \frac{(1 - x) \cdot A^0_{tot}}{\lambda_{Y}} \right) \cdot e^{\lambda_{Y} \cdot t} \tag{4.14}
\]

LSC measurements provide measured total solution activities; Equations 4.12 and 4.14 are converted to activities instead of atoms using Equation 4.7, leading to Equations 4.15 and 4.16.

\[
A_{Sr} = x \cdot A^0_{tot} \cdot e^{\lambda_{Sr} \cdot t} \tag{4.15}
\]

\[
A_{Y} = \left( \frac{x \cdot A^0_{tot}}{\lambda_{Y} - \lambda_{Sr}} \right) \cdot \left( e^{\lambda_{Sr} \cdot t} - e^{\lambda_{Y} \cdot t} \right) \cdot \lambda_{Y} + \left( \frac{(1 - x) \cdot A^0_{tot}}{\lambda_{Y}} \right) \cdot e^{\lambda_{Y} \cdot t} \tag{4.16}
\]

The sample is isotopically pure and Equation 4.3 can be used to combine Equations 4.15 and 4.16 to give Equation 4.17.

\[
A_{tot} = x \cdot A^0_{tot} \cdot e^{\lambda_{Sr} \cdot t} + \left( \frac{x \cdot A^0_{tot}}{\lambda_{Y} - \lambda_{Sr}} \right) \cdot \left( e^{\lambda_{Sr} \cdot t} - e^{\lambda_{Y} \cdot t} \right) \cdot \lambda_{Y} + \left( 1 - x \right) \cdot A^0_{tot} \cdot e^{\lambda_{Y} \cdot t} \tag{4.17}
\]

This equation has three unknown parameters: initial total activity, final total activity, and the ratio \( x \).

Over the course of several days (2-21 days), the sample is counted multiple times. The counts and the times at which they occur are plotted in the software OriginPro 2015, with the assumption that the first count was \( A^0_{tot} \) and occurred at \( t = 0 \). This plot for measured total activity as a function of time is then fitted with a non-linear curve fit. The curve fitting and Equations 4.5 and 4.6 provide the \( x \) ratio for the initial measured activity and the initial Sr and Y activities can be determined using the measured total initial activity.
Method Validation

Two different studies were conducted to test the technique. In the first study, $10^{-5}$ M Sr and $10^{-5}$ M Y in 0.1 M NaClO$_4$ buffered at pH 5.5 with 1 mM MES buffer was spiked with $^{90}$Sr/$^{90}$Y to obtain an activity of approximately 250 Bq/mL. This solution was contacted with $10^{-2}$ M HEHEHP in dodecane for 2 hours (determined to be a sufficient time to reach equilibrium) on an orbital shaker. HDEHP will preferentially extract trivalent Y into the organic phase, leaving the Sr in the aqueous phase, shifting both organic and aqueous phases away from secular equilibrium in opposite directions. The samples were then centrifuged for 5 minutes at 3,000 rpm and then 1 mL aliquots of both phases were added to 4 mL of Ecoscint Original. These samples were counted daily for 21 days. At 21 days, the samples would have achieved secular equilibrium and the measured activity beyond that point could be used to calculate the specific $^{90}$Sr and $^{90}$Y activities to compare to the curve fitting technique.

The second validation technique consisted of conducting ligand dependence studies with TTA; one set of experiments were conducted using $^{90}$Sr and $^{90}$Y radioisotopes and the second experiment set employed stable Sr and Y. This technique sought to compare the distribution values calculated using stable and radiotracer solvent extraction studies, providing a means to compare the Bateman derived technique with stable element ICP-OES analysis. The total activity of the radiotracer samples were measured using LSC and individual activity of $^{90}$Sr and $^{90}$Y were calculated using the Bateman equation; Sr and Y concentrations in the stable samples were measured using ICP-OES (both aqueous and organic, as explained in Chapter 3 and Appendix A). The resulting ligand extraction mechanism from both experiment sets (radiotracer and stable isotopes) were then compared. In these studies, stable isotope samples contained an aqueous phase of $10^{-5}$ M Sr and $10^{-5}$ M Y in 0.09 M NaClO$_4$ with 0.01 M acetate buffer at pH 4, the organic phases consisted of 0.02 – 0.1 M TTA in xylenes. The two phases were contacted for 2 hours on an orbital shaker, centrifuged for 5 minutes at 3,000 rpm, and 1 mL aliquots of each phase were sampled for ICP-OES analysis. The organic stable aliquots were diluted with $10^{-2}$ M
HDEHP in dodecane and analyzed using ICP-OES; the aqueous stable aliquots were diluted with 2% HNO₃ and analyzed with ICP-OES. The radiotracer studies consisted of an aqueous phase containing 150 Bq/mL ⁹⁰Sr/⁹⁰Y, 10⁻⁵ M Sr, 10⁻⁵ M Y, 0.09 M NaClO₄, with 0.01 M sodium acetate as buffer at pH 4, the organic phases consisted of 0.02 – 0.1 M TTA in xylenes. The radiotracer aliquots were added to 19 mL of Ecoscint Original and counted for 5 minutes several times over the course of 3 days. The Dilution of 1 mL 0.1 M TTA with 19 mL scintillation fluid prevented any quenching from occurring during counting.

Using the concentrations determined for each phase, the distribution coefficients were determined using Equation 4.18. These calculated values were then plotted against the concentration of TTA for ligand dependence.

\[
D = \frac{\sum [M]_{\text{org}}}{\sum [M]_{\text{aq}}} \tag{4.18}
\]

**Results and Discussion**

**Curve Fitting Results**

Using the first set of radiotracer data (using the extractant HEHEHP), the Bateman derived function was tested with the aqueous and organic phases from one sample and the uncontacted aqueous aliquot. The samples were counted with LSC daily for 22 days, yielding the plot shown in Figure 4.1.
Figure 4.1. Activities of organic (Blue Squares) and aqueous phases (Green Triangles) from $10^{-5}$ M Sr and $10^{-5}$ M Y contacting $10^{-2}$ M HEHEHP at pH 5.5; the red circles are an aliquot of uncontacted aqueous phase to show initial activity, and the dashed lines are each $^{90}$Y half-life.

Before fitting these data with the Bateman derived function, several observations can be made. 1) The uncontacted aqueous phase had not quite reached equilibrium at the time of the study, this was most likely due to the tracer being acidified prior to use and the time between acidifying and spiking the solution was not adequate for both the $^{90}$Sr and $^{90}$Y to completely dissolve in solution. 2) The organic phase contains both $^{90}$Sr and $^{90}$Y, with $^{90}$Y accounting for the majority of the activity; this is shown by the decrease in total activity (12 to 7 Bq). 3) The aqueous phase consists primarily of $^{90}$Sr and the later counts show the ingrowth of $^{90}$Y as secular equilibrium is achieved. While these conclusions are helpful in understanding concepts, we want to derive exact values.
To obtain the exact $^{90}$Sr-to-Total activity ratio (x, as shown in Equation 4.4), Equation 4.17 was fitted using OriginPro 2015’s nonlinear curve fit to each of the three data sets shown in Figure 4.1 (the exact details of the non-linear curve fitting are listed in Appendix D). The resulting curve fits are shown in Figure 4.2, Figure 4.3, and Figure 4.4.

![Graph showing non-linear curve fit](image_url)

**Figure 4.2.** Non-linear curve fit for the uncontacted aqueous phase of $10^{-5}$ M Sr and $10^{-5}$ M Y.
Figure 4.3. Non-linear curve fit for the aqueous phase of $10^{-5}$ M Sr and $10^{-5}$ M Y after contacting $10^{-2}$ M HEHEHP in dodecane.

Figure 4.4. Non-linear curve fit for $10^{-2}$ M HEHEHP in dodecane after contacting $10^{-5}$ M Sr and $10^{-5}$ M Y.
The three previous figures show the fits for each data set and all have an $R^2$ value of at least 0.99. However, the most important piece of data is the x values reported with the fitting, which provide the fraction of the initial activity that was due to $^{90}\text{Sr}$. Using the x values (Sr to total activity ratio) calculated after 22 days of daily LSC, and the initial total activities determined with LSC, the individual initial activities for $^{90}\text{Sr}$ and $^{90}\text{Y}$ were determined. The three sample types used where the uncontacted aqueous phase (Figure 4.2), contacted aqueous phase (Figure 4.3), and the contacted organic phase (Figure 4.4); since HEHEHP extracts Y and not Sr, the organic phase consists of primarily $^{90}\text{Y}$ while the contacted aqueous phase has depleted $^{90}\text{Y}$ activities compared to the uncontacted aqueous phase. While the extraction system used for this study is not optimized, data show that the Bateman derivation is a good fit for the $^{90}\text{Sr}/^{90}\text{Y}$ behavior, regardless of the initial ratio.

**Method Validation – Secular Equilibrium**

The set of radiotracer samples that were counted for the method validation (using the HEHEHP extractant, at a concentration of $10^{-2}$ M, which we found provided satisfactory distribution between the two phases) over the course of 22 days was background corrected; the time (in seconds) and background corrected activities were fitted with Equation 4.17. The fitting function provided x-values for each sample, where x is the ratio of $^{90}\text{Sr}$ to total activity at the time of the first count, as described above. The count at 22 days was used to determine the final activities. At 22 days, the samples will have achieved secular equilibrium, so in a background corrected sample, 50 percent of the activity would be due to $^{90}\text{Sr}$ and 50 percent would be due to $^{90}\text{Y}$. With these final activities, the activities at the point at which contact was ended can be back calculated.
To gauge the precision of the curve fitting technique, the ratios calculated from the final (day 22) counts were compared to the ratios calculated with each set of count data as it was fitted with the function. The percent differences between the curve fit calculated x-values and the secular equilibrium calculated x-values were calculated. These are shown in Figure 4.5, where the y-axis is the average percent difference for the total set of nine samples compared to their ratios calculated once the samples had sufficient time to achieve secular equilibrium. The x-axis is the number of count days (i.e. at x = 5, the samples had been counted on 5 separate consecutive days).

![Average percent difference between the 90Sr to total activity ratio calculated via the Bateman derivation curve fitting function and from the final secular equilibrium plotted versus the number of count days, error bars are 1σ.](image)

**Figure 4.5.** Average percent difference between the $^{90}$Sr to total activity ratio calculated via the Bateman derivation curve fitting function and from the final secular equilibrium plotted versus the number of count days, error bars are $1\sigma$. 
Even after just 2 count days, the average percent difference is less than 2 percent. Counting over the course of 5 days decreases the average percent difference to essentially zero with a standard deviation of less than 2. Typically counting methods (without separations) require the samples to achieve secular equilibrium before an accurate value can be determined. Being able to gain an approximate value in two days and an accurate value in less than 1 week is a drastic improvement, compared to 3 weeks required for secular equilibrium to be achieved. The error in the initial counts is likely due to the fact that there is an insufficient change in activity to accurately determine the trend. Beyond 1 week, the standard deviation between replicates (when compared to the ratio calculated when secular equilibrium had been achieved) is very consistent and is likely due to the variation found within LSC counting.

Method Validation – Ligand Dependence Comparison

The results of the ligand dependent study with either only stable isotopes or radiotracer with cold carrier samples are shown in Figure 4.6. Under the conditions of this study, no significant concentrations of Sr were detected in the organic phase by LSC or ICP-OES. The Sr and Y radiotracer concentrations were derived using the Bateman curve fitting function and the stable Sr and Y concentrations were quantified using ICP-OES for both the aqueous and organic phases. We observed a shift of D values between the stable and radiotracer sample sets. This difference is potentially due to differences in the aqueous phases. The radiotracer spike of $^{90}\text{Sr}^{/90}\text{Y}$ was in HClO$_4$ to ensure the Sr and Y stayed in solution without sorbing to the vial. After the addition of the radiotracer, the solution had to be brought back up to pH 4 with NaOH. With the addition of NaOH, there may have been localized hydrolysis that occurred with the Y. Overall though, the Bateman derived concentration values based on LSC data provided a similar trend compared to the study conducted with stable metals and ICP-OES quantification.
Figure 4.6. Comparison of ligand dependent slope analysis studies for spiked and stable solutions of $10^{-2}$ M Y and $10^{-5}$ M Sr in 0.1 M NaClO$_4$ buffered at pH 5.5 with 1 mM MES buffer contacting $10^{-2}$ M HEHEHP in dodecane. Spiked solutions were quantified using the Bateman derived curve fitting and stable solutions were quantified using ICP-OES.

Under acidic conditions ($\text{pH} \leq 2$), the ligand dependent slope of TTA has a slope equal to the charge of the metal being extracted; extractions of trivalent metals such as Y exhibit a slope of 3.$^{32}$ When the pH is increased above 2, the slope of the ligand dependence plot gradually decreases. This change is believed to be partially due to the increase in the aqueous phase solubility of TTA as pH increased. The slopes of both the stable and radiotracer experiments were similar to those reported in the literature under non acidic conditions.$^{33}$
Conclusion

Even with only 2 days of count data, the Bateman derived ratios had a similar deviation from the secular equilibrium values as Cherenkov counting exhibits.\textsuperscript{23} Counting multiple times over the course of 1 week drastically decreases the differences and the deviation between individual samples. This method demonstrates an improvement compared to commonly used methodology, with 1 week of counting being much faster than waiting for complete secular equilibrium to be reached; this method saves 1 - 2 weeks of counting time. Additionally, no chemical separation or deconvolution is required to determine the individual $^{90}$Sr and $^{90}$Y activities.
References


32. Friend, M.; Wall, N., Hafnium(IV) complexation with oxalate at variable temperatures. 


The studies described in this body of work better characterize separation techniques and developed improved quantification methods for fission products. Strontium and its daughter, $^{90}\text{Y}$, are very important isotopes for both nuclear forensics and environmental monitoring. Due to their radioactive decay properties, traditional analytical techniques rely on separations prior to quantification. These studies sought to improve the understanding of two of the popular solid phase extraction techniques and develop new quantification methods that do not rely on traditional time-consuming pre-analysis sample treatment.

Solid phase extraction is one of the most commonly used separation techniques for the isolation of individual fission products. The two primary products available for Sr separation are Eichrom’s Sr Resin and IBC Advanced Technologies’ Analig® SR-01. While both resins are commonly used in analytical laboratories, there were no direct comparison data between the two resins. Without a direct comparison, it was not possible to determine which resin offers better separation for the purification and isolation of Sr. The two resins were compared under identical conditions in order to get weight distribution ratios which were used to evaluate the resin abilities to separate Sr from Ba. With weight distribution ratios, the two resins efficacies can be compared even though they have completely different design (supporting media composition and the ligand itself).

Quantification of $^{90}\text{Sr}$ and/or $^{90}\text{Y}$ typically requires separations prior to counting or waiting until the $^{90}\text{Y}$ has ingrown to the point of secular equilibrium. These methods provide accurate results but the disadvantages are that the separations are time consuming and can be costly depending upon on the separation methods used. Using a derivation of the Bateman Equation and the secular equilibrium of $^{90}\text{Sr}$ and $^{90}\text{Y}$, a new technique was developed that does not require separation of $^{90}\text{Sr}$ and $^{90}\text{Y}$ or the complete
ingrowth of $^{90}$Y. When a sample only contains $^{90}$Sr and $^{90}$Y, the change in activity occurs according to a predictable trend. Using this trend and the derivation of the Bateman Equation, the activities of $^{90}$Sr and $^{90}$Y can be determined with a curve fitting function. This technique decrease the time required for analysis without requiring additional separations or analytical tools.

One of the studies presented in this document describes a potential improvement on the methodology for the analysis of non-traditional solutions using ICP-OES. ICP-OES is an analytical tool that is readily available in many laboratories. Typically it is used for the analysis of metals in dilute acid solutions. We developed methodologies for analyzing both high salt solutions (up to 5 m) and organic solvents. Extreme condition sample processing can now be drastically decreased prior to analysis, decreasing analysis time and cost per sample. This development will be beneficial for solvent extraction studies. Typically solvent extraction studies imply the use of radiotracers and both phases can be readily analyzed via radiometric counting. Thanks to this new development, both phases can be analyzed using ICP-OES, removing the need for radioactive material, decreasing the cost and reducing the environmental impact.

In addition to these primary pieces of work, several additional studies were performed to improve analytical techniques in conjunction with preliminary studies for the interaction of fission products with naturally occurring colloids. Two new characterization techniques were developed to improve the characterization of humic acid – an ashing technique with greatly improved precision and metal impurity analysis using TXRF, as described in the following appendices.

**Future Work**

While the studies conducted opened up the potential to analyze a far broader range of solutions using ICP-OES, there is the potential for a number of further studies. The techniques described in this body of work are limited by the volatility of the organic solvents and the molecular emissions. As the volatility
increases, more of the solvent is transferred to the torch, ultimately leading to plasma stability issues or simply the plasma extinguishing. Depending on the specific wavelength of the analytes, the molecular emissions peaks can have no influence, but can also cause a drastic shift of the detection limits. Further studies could be conducted better characterizing the influence of organic solvent type of analysis and techniques to increase the range of solutions that can be analyzed. It appears that the level of oxygen added to the plasma system influences the molecular emissions, but further characterizations are needed to understand the time at which it should be added and the percentages to use to obtain the best detection limits. With these two further sets of studies, the utility of ICP-OES can be further improved for the analysis of organic solutions.
APPENDIX A

INDUCTIVELY COUPLED PLASMA OPTICAL EMISSION SPECTROMETRY

Introduction

Two ICP-OES instruments were used to complete this research. A Perkin Elmer Optima 3200 RL ICP-OES Running WinLab32 for ICP, version 3.4 (Perkin Elmer, Waltham, MA) was used for the research detailed in Chapter 2. And an Agilent 5100 SVDV ICP-OES with an SPS 3 auto-sampler with a 1.3 mm interior diameter inert PTFE sleeved probe and running ICP Expert Version 7.1.0.6821 (Agilent Technologies, Santa Clara, CA). The largest portion of this research was completed using the Agilent instrument, so the Perkin Elmer will only be mentioned briefly.

Instrument Set Up

Perkin Elmer

The 3200 uses a radial quartz torch with a removable alumina injector. This assembly is coupled with a plastic Scott type spray chamber, with the nebulizer built in. Only aqueous solutions in dilute acid were analyzed on this instrument.

Agilent

A number of different setups were used with the 5100, so that a variety of different solution matrices could be analyzed. Chapters 3 and 4 detail the quantification of a variety of metals in a variety of media types; the specific components used in the analyses are listed in Table A.1. With organic solution analysis, using the correct torch and nebulizer is important in order to ensure that the solvent is nebulized and not vaporized, and to limit the amount being injected into the plasma (done via the smaller injector diameter of the organic torch). If large quantities of the organic solvent are vaporized and/or injected into the plasma, the increased energy required to ionize the organic molecules can cause the plasma to stutter.
or extinguish. Additionally, the other important component to switch out when analyzing organic solutions is the pump tubing. PVC tubing is typically used for analyzing aqueous solutions due to its durability and low cost, but PVC is incompatible with many organic solvents. We found that Solva Flex tubing offered the best combination of long life span and solvent resistance. For tubing where consistent flow rate is not as essential, such as the waste and rinse lines, other tubing types such as Viton can be used in order to decrease operating costs. Regardless of the tubing or solvent, the tubing must be regularly inspected to insure there is adequate and consistent flow.

Table A.1. Consumable components used on the Agilent 5100 for analysis of aqueous and organic solutions.

<table>
<thead>
<tr>
<th></th>
<th>Aqueous Solutions</th>
<th>Organic Solutions</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Torch</strong></td>
<td>1.8 mm injector, one piece Torch</td>
<td>1.4 mm injector, demountable Torch</td>
</tr>
<tr>
<td></td>
<td>Agilent G8010-60228</td>
<td>Agilent G8010-60233</td>
</tr>
<tr>
<td><strong>Spray Chamber</strong></td>
<td>Twister Spray Chamber with helix, Glass Expansion 20-809-9199HE</td>
<td></td>
</tr>
<tr>
<td><strong>Nebulizer</strong></td>
<td>SeaSpray 2mL/min, Glass Expansion A14-07-USS2</td>
<td>Conikal 2mL/min, Glass Expansion A14-07-UC2</td>
</tr>
<tr>
<td><strong>Pump Tubing Material</strong></td>
<td>PVC</td>
<td>Solva Flex</td>
</tr>
</tbody>
</table>

In addition to switching out the parts for organic solution analysis, using an auxiliary gas is necessary. A mixture of 20% oxygen and 80% argon is connected to the auxiliary gas port and set for 1 mL/min flow in the software. Adding oxygen to the plasma allows for the formation of COx gases as the organic molecules are ionized in the plasma. This decreases the formation of carbon deposits and increases precision and longevity of the instrument. Without the additional oxygen, carbon build-up will occur on the injector, torch body, and the instrument chamber above the torch. With sufficient build-up, eventually
the sample flow can become obstructed and in extreme cases, the carbon build-up can be great enough to obstruct the windows to the detector, decreasing measured signals.

**Instrument Warm up**

Both instruments require significant warm up time between igniting the plasma and starting sample analysis. The measured intensity of 10 ppm Y standard sample measured repeatedly on the Perkin Elmer ICP-OES is shown in Figure A.1. The measured intensities do not begin to stabilize until approximately 60 minutes. For all analyses with this instrument, the plasma was allowed to warm up for 90 minutes prior to samples being analyzed.

![Figure A.1](image)

Figure A.1. Measured intensities of a 10 ppm Y standard, starting immediately after plasma ignition.

In the case of the Agilent 5100, many more variables could be recorded to ensure the instrument has fully stabilized before any analysis is done. A set of identical samples of 5 ppm Sr in 2% HNO₃ was prepared and analysis was started immediately following plasma ignition. During this sample analysis, nebulizer
pressure, intensity of the Ar emission, and intensity of the Sr emission were all recorded for each sample. The nebulizer pressure (Figure A.2) continued to increase until approximately 50 minutes after sample ignition and then slowly stabilized completely after approximately 75 minutes. The Ar intensity (Figure A.3) exhibited the opposite trend, decreasing for 20 minutes and then leveling off. The Sr intensities (Figure A.4) varied for the first 50 minutes before changing to gradual drift. This emphasizes the need to run calibration checks during longer sample runs; even if the solutions are stable and the plasma has been allowed to warm, there will be some instrumental drift during longer runs. In order to avoid issues with the instrument not having stabilized, for all analyses, the plasma was ignited and then allowed to run for a minimum of 60 minutes before any samples were analyzed.

![Graph showing nebulizer pressure over time](image)

**Figure A.2.** Nebulizer pressure for a sample set starting immediately after plasma ignition.
Figure A.3. Instrument reported Ar intensities over the course of the run; no wavelength was specified.

Figure A.4. Measured intensities of the 421.552 nm emission of a 5 ppm Sr solution repeated continually following the ignition of the plasma. Errors are 3σ, calculated from triplicate measurements.
Detection Limits

When quantifying an element that has not been analyzed before on the same instrument, the first step is to determine an approximate limit of detection (LOD). To do this, a series of samples were prepared with concentrations ranging from 1 ppt to 100 ppm ($10^{-6} - 100 \text{ µg·mL}^{-1}$). These samples were run along with several 2% HNO₃ blanks. As an example, the process used to determine the LOD and Limit of Quantification (LOQ) for Ce will be covered. Shown in Figure A.5 are the intensities of the top 5 emission lines of cerium recommend by the instrument software. The concentrations below 0.01 ppm are not distinguishable from the blanks (blanks’ intensities are shown as horizontal lines) and the 0.01 ppm solutions’ intensities are approximately one order of magnitude higher than the blanks. For time saving, if prior analyses have been done with the same element, those can be used to determine an approximate LOD.

**Figure A.5.** Approximation of the limit of detection for the top 5 Ce emission lines; the horizontal lines are the intensities of the blanks for each wavelength.
With this information, the LOD and LOQ can be determined for Ce using the method from *Quantitative Chemical Analysis*. In summary, a solution is prepared that is between one and five times the approximate detection limit. This solution is analyzed with $n$ ($n > 6$) replicate samples, along with $n$ blanks and a linear calibration curve. The signal detection limit is calculated using A.1, where $s$ is the standard deviation of the $n$ low-concentration replicates.

$$y_{dl} = y_{blank} + 3 \cdot s \quad \text{A.1}$$

If the signal is background corrected, it is proportional to the sample concentration, as shown in equation A.2, where $m$ is the slope of the calibration curve.

$$y_{sample} - y_{blank} = m \cdot (\text{sample concentration}) \quad \text{A.2}$$

Equations A.1 and A.2 can be combined to provide the LOD in terms of sample concentration (Equation A.3).

$$\text{LOD} = \frac{3 \cdot s}{m} \quad \text{A.3}$$

For non-traditional solution analysis, additional techniques for LOD determination are detailed in Chapter 3. While the LOD provides a concentration that is detectable above background, this is not a sufficient difference for quantitative measurements. As shown in Figure A.6, a sample at this concentration has a 50 percent chance of being below the LOD (blue area) and a sample at background levels has a one percent chance of being measured as above the LOD (small area to the right of the $y_{dl}$ line).

To avoid both false positives and false negatives, the LOQ is placed at 10 standard deviations away from the signal of the blanks, yielding Equation A.4.

$$\text{LOQ} = \frac{10 \cdot s}{m} \quad \text{A.4}$$
**Figure A.6.** Probability distributions of a blank ($y_{\text{blank}}$), a sample at the detection limit ($y_{\text{dl}}$, 3σ), and a sample at the quantification limit ($y_{\text{ql}}$, 10σ). The blue region is the region where a sample at the detection limit would be mistaken for a sample having a concentration of 0 (50% chance) and the small region to the right of the $y_{\text{dl}}$ line is where a sample with a concentration of 0 would be mistaken for having a concentration above the detection limit (1% chance).

In the case of the Ce LOD and LOQ determination, Figure A.5 shows that the detection limit is somewhere around 0.01 ppm and the 418.659 nm line has the highest intensities. For determining the best available LOQ for Ce, the 418 nm line was used. To err on the side of caution, a solution of 0.05 ppm Ce in 2% HNO$_3$ was prepared. Ten replicates of this solution, ten 2% HNO$_3$ blanks, and a calibration curve ranging from 0.07 to 1 ppm were all prepared and analyzed on the ICP-OES. The resulting intensities are shown in Figure A.7. Using the slope of the linear calibration and the standard deviation of the 10 replicates of 0.05 ppm Ce, the LOD and LOQ were determined to be 0.0013 and 0.0045 ppm, respectively, via Equation A.4.
Figure A.7. The resulting intensities of the 418.659 nm emission line of Ce; the linear calibration (black points), average of 10 replicates of 0.05 ppm Ce (red point), and average of 10 blanks (green point).

For single element quantification in aqueous solutions, selecting the emission line associated with the best detection limit is a fairly simple process. If more than one element is present in the samples, the emissions lines need to be checked to make sure there is no overlap between the targeted elements. The solvent or supporting electrolytes can contribute to the background and correspondingly the detection limits; make sure the checks are done with the same media as will be present in the samples. When analyzing organic solvents, the high carbon content leads to molecular emission peaks from CN and C₂ molecules that are formed in the plasma (a list of some of the problematic molecular emission peaks is available in Table A.2). As long as the lines being analyzed do not overlap with the regions of the molecular emissions, there is no effect. However, if there is overlap, the detection limits can be
drastically affected. In the case of Sr, the primary peaks overlap the molecular emissions region, which decreases the detection limits by several orders of magnitude. Whenever working with a new element or solvent, it is recommended to always perform an LOD/LOQ check to insure the switch has not negatively affected the analysis method. As detailed in Chapter 3, even something as minor as changing the length of the alkane solvent will affect the volatility of the solvent which can then change the measured intensities of the molecular emissions.

Table A.2. Common molecular species and their emissions lines that can occur during the analysis of high carbon content solvents.²

<table>
<thead>
<tr>
<th>Species</th>
<th>Emission Lines</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₂</td>
<td>436.52 437.14</td>
</tr>
<tr>
<td></td>
<td>438.25 467.86</td>
</tr>
<tr>
<td></td>
<td>468.48 469.76</td>
</tr>
<tr>
<td></td>
<td>471.52 473.71</td>
</tr>
<tr>
<td></td>
<td>512.93 516.52</td>
</tr>
<tr>
<td></td>
<td>547.03 550.19</td>
</tr>
<tr>
<td></td>
<td>554.07 558.55</td>
</tr>
<tr>
<td></td>
<td>563.55</td>
</tr>
<tr>
<td>CH</td>
<td>431.25 431.50</td>
</tr>
<tr>
<td>CN</td>
<td>358.38 358.59</td>
</tr>
<tr>
<td></td>
<td>359.04 385.09</td>
</tr>
<tr>
<td></td>
<td>385.47 386.19</td>
</tr>
<tr>
<td></td>
<td>387.14 388.34</td>
</tr>
<tr>
<td></td>
<td>415.34 416.78</td>
</tr>
<tr>
<td></td>
<td>418.10 419.70</td>
</tr>
<tr>
<td></td>
<td>421.60</td>
</tr>
</tbody>
</table>
**Sample Analysis**

*Solution Preparation*

Traditional ICP-OES sample quantification is performed in a dilute mineral acid, typically 1-2% HCl or HNO₃. This is done not for the instrument but to insure the metal analyte is stable and stays in solution. If acidification of an aqueous sample is not an option (e.g. due to precipitation), neutral solutions can be analyzed. For instance, 0.1 M NaCl solutions can be analyzed without acidification if there are dilution or solubility concerns. When analyzing non-traditional aqueous solutions, we make sure the standards are prepared in the same media as the samples. Additionally, analysis of solutions with high Na content (above approximately 0.05 M) leads to expedited wear of the quartz on the torch. The only way to avoid this is to dilute the sample, so when possible, dilution and acidification is usually the best option for increased sample stability and maintaining the instrument. In extreme cases, up to molal concentrations of salt can be analyzed, this is further detailed in Chapter 3. In review, it is possible to quantify metal analytes in 5 m NaCl, but due to the drastically increased wear on the instrument consumables and salt build-up, it is discouraged for all but the most exigent circumstances.

For organic solutions, Chapter 3 presents an in-depth demonstration of the instrumentation behavior associated with the addition of an organic complexant to the organic phase. Without the addition of an organic complexant, such as HDEHP, the metal analyte may not stay in solution and the rinse solutions will be much less effective, especially compared to the aqueous rinse solutions. The addition of the complexant allows for standards and samples to have an increased shelf life and allows for rinse times to be kept fairly brief while still preventing any carry over between samples.

For typical sample analysis, knowledge of the approximate range of concentrations possible is crucial for obtaining accurate data. Without knowledge of the concentration range, an accurate calibration curve cannot be obtained. Furthermore, if the samples are too concentrated, they can overwhelm the detector
and increase the risk of sample carry over. Shown in Figure A.8 is the resulting spectrum when a signal overwhelms the detector. The signal is too high for the detector to completely resolve the peak without being overwhelmed – preventing the completed emission peak from being resolved. When a sample overwhelms the detector, the top of peak is typically cut-off, leading to an elongated “Batman” silhouette, as seen in the spectrum below, preventing any accurate measurements from being made.³

![Graph showing a spectrum with a peak that has been overwhelmed by the detector.](image)

**Figure A.8.** Spectrum of a 100 ppm Sr solution with the 421.552 nm emission line that has overwhelmed the detector.
Troubleshooting

Plasma Not Igniting

When the plasma is not igniting, the first thing to always check is the Ar level. We make sure there is adequate flow and no leaks. If that does not resolve the issue, we check all of the components and make sure everything is properly fitted. If oxygen is getting into the system, the plasma will not ignite. On the Perkin Elmer, we remove the ignitor rod and clean it with water and then polish it with fine sand paper; if its surface is too oxidized, it will not ignite the plasma. On the Agilent, typically the most common problem is Ar flow or oxygen in the system. If it recently had components switched out, there is most likely residual oxygen in the system. If this is the case, we simply keep trying to ignite the plasma and it will eventually flush itself out and light.

Intensity Fluctuations

If the intensity of the plasma is fluctuating, there are several possible causes:

1) The Ar supply is running low but is not yet low enough to trigger alarms.

2) The nebulizer is clogged. Check the flow out of the nebulizer and make sure it is giving consistent flow. The nebulizer can be rinsed with dilute acid to clean it and isopropanol to help dry.

3) The peristaltic pump tubing is worn down. Check the tubing and make sure it has no flat spots. If it has flat spots where it contacts the pump, it needs to be replaced.
References


APPENDIX B
EXTRACTANT PURIFICATION

Impurities present in commercially available extractants may only represent a small fraction of the sample, but may also influence chemical behaviors in an uncontrolled manner. The nature of impurities may be unknown and may not be consistent between different lot numbers or as the reagent ages. For example, TTA ought to be stored at temperature under 10°C and it is safe to assume that it is not stable at room temperature; in fact visible color impurities are a clear sign that degradation occurs over time. If there is variation between lots, the data derived from the solvent extraction studies would all have increased uncertainty. By purifying the extractants, one of the sources of error can be decreased to the point of being negligible.

HDEHP

The purification used was based on a method originally from Partridge and Jensen. Seventy g of copper sulfate pentahydrate (CuSO₄·5H₂O) was dissolved in a flask with approximately 250 mL degassed H₂O. Thirty grams HDEHP was combined with 100 mL diethyl ether and the ether and water solutions were mixed in a separatory funnel. While the mixture was stirring, 8 g of saturated sodium hydroxide (NaOH) solution was added dropwise. With the addition of the NaOH, the following two reactions occur:

\[
\text{CuSO}_4 + 2\text{NaOH} \rightarrow \text{Cu(OH)}_2 + \text{Na}_2\text{SO}_4 \quad \text{B.1}
\]

\[
\text{Cu(OH)}_2 + 2\text{HDEHP} \rightleftharpoons \text{Cu(DEHP)}_2 + 2\text{H}_2\text{O} \quad \text{B.2}
\]

The CuSO₄ reacts with the NaOH to form copper hydroxide (Cu(OH)₂) and then the Cu(OH)₂ reacts with the HDEHP in the organic phase to form copper di-(2-ethylhexyl)phosphate, which remains in the organic phase. NaOH must be added slowly to allow for the Cu(OH)₂ to react with the HDEHP, otherwise CuO can form as a black precipitate in the organic phase. Once all of the NaOH had been added, the solution was stirred for approximately 8 hours to ensure all of the HDEHP had reacted with the Cu(OH)₂.
After sufficient mixing, the two phases were separated, saving the organic phase. The ether solution containing Cu(DEHP)$_2$ was gently heated to evaporate most of the diethyl ether, reducing the solution volume by approximately 75%. Acetone was then added to the solution while stirring, until no more Cu(DEHP)$_2$ precipitated (a light blue solid). The precipitated Cu(DEHP)$_2$ was collected via filtration and rinsed with acetone. The collected precipitate was combined with 200 mL 3 M HCl. The addition of HCl causes the following reaction to occur and two phases will form.

\[
\text{Cu(DEHP)}_2 + 2\text{HCl} \rightleftharpoons 2\text{HDEHP} + \text{CuCl}_2
\]

The aqueous phase is the H$_2$O and unreacted CuSO$_4$ and Cu(OH)$_2$ and the organic phase consists of the HDEHP oil. Twenty mL of 3 M HCl was added to allow for complete protonation of the HDEHP, and 20 - 30 mL of ether was added to allow for a more easily distinguished organic phase. After mixing, the aqueous phase was decanted. Degassed DI water (approximately 2 times the volume of the HDEHP phase) was added to remove any remaining aqueous acid. The solutions were mixed and the aqueous phase was decanted again; this was repeated twice more to insure complete removal of the aqueous acid. Following the mixing of the rinse solution, the mixture was allowed to settle for up to an hour to allow the emulsion formed at the interface to separate. After the three washes, the HDEHP oil and ether solution was transferred to a 50 mL centrifuge tube with anhydrous magnesium sulfate (MgSO$_4$) to remove any residual water. The mixture was then centrifuged to separate the MgSO$_4$ from the HDEHP/ether solution.

After the solution had been adequately dried, it was transferred to a round bottom flask and was placed on a rotovap to remove the ether. The vacuum was slowly increased while the bath was kept at 25°C for the first 15 minutes. Then the water bath was slowly ramped up to 60°C to remove the remaining ether.
Phosphorus-31 NMR was performed on both the unpurified and purified HDEHP. Shown in Figure B.1 is the $^{31}$P spectrum of the unpurified Alfa Aesar HDEHP, the small peaks on either side of the primary peak are phosphoric containing impurities. Figure B.2 shows the HDEHP following the purification process. The magnified inset of the purified HDEHP shows that there are no other peaks, even when zoomed in more than in Figure B.1. The absence of any other peaks confirms that the purification was successful and the other phosphoric acid derivatives have been removed.

![Figure B.1](image)

**Figure B.1.** $^{31}$P NMR of unpurified Alfa Aesar HDEHP, with a magnified inset showing the two peaks due to impurities.
Figure B.2. $^{31}$P NMR of the Alfa Aesar HDEHP following purification, the magnified inset is showing the absence of any peaks resulting from impurities.

HEHEHP

The HEHEHP was purified using an extraction procedure from Hu et al.² Five hundred mL of a 20% by volume solution of HEHEHP in hexanes was contacted with 500 mL of a 1 M NaOH, 0.15 M Na$_2$SO$_4$ solution. This converts the HEHEHP to its sodium salt and forms a third phase. After allowing the mixture to settle for several hours, the middle phase is collected. Five hundred milliliters of 6 M HCl is added to the collected middle phase, converting the HEHEHP back to its acid form. The re-acidified and purified HEHEHP is in the organic phase. Depending on the starting purity of the HEHEHP, these two steps may need to be repeated multiple times. After the final acidification, the organic phase is washed with five 100 mL rinses of deionized water to remove any remaining HCl. The organic phase is centrifuged to separate any emulsion that may have formed with water. Na$_2$SO$_4$ is added to remove the
last of the remaining water. The Na₂SO₄ is removed via centrifugation and then a rotovap is used to remove the hexanes. The final product is the HEHEHP oil.

**TTA**

A simple recrystallization is typically done to purify TTA.³ A sample of TTA was dissolved in near boiling toluene. Due to the relatively high solubility levels of TTA in toluene, simply decreasing the temperature in an ice bath was not sufficient to prompt significant recrystallization. To allow for a higher yield recrystallization, the TTA/toluene solution was placed in a vacuum freeze-drier (Labconco FreeZone 1 Liter Benchtop Freeze Drier, Kansas City, MO). Once vacuum was applied, the toluene began evaporating. When sufficient toluene had evaporated, the TTA began to crystallize. At this point the mixture was removed from the freeze drier and the TTA crystals were collected. This process was repeated until sufficient TTA had been collected.

Prior to recrystallization, the solid TTA ranged in color from white to a reddish orange shade. Following recrystallization, the collected crystals were a creamy white color once they had been sufficiently dried. No further purity analysis were done on the TTA; if the crystals no longer had color impurities it was assumed that they were pure.
References


APPENDIX C

NEAR NEUTRAL SOLVENT EXTRACTION STUDIES

Introduction

The elements Sr and Y are high yield fission products (approximately 5-6% cumulative yields for the 90 isobar). Radioactive elements release to the environment constitutes a concern from the standpoint of health hazard (for example, $^{90}$Sr can replace Ca in the bone, leading to a drastically increased risk of cancer) and accurate measurements are required for environmental protection. The detection of Sr and Y also constitutes an asset for nuclear nonproliferation; their high yield provides a tool for signature development. Better understanding of the interaction of Sr and Y with naturally occurring molecules allows for better characterization of the environmental fractionation that would occur in the case of a nuclear event.

Natural groundwaters typically feature a neutral pH, ranging from approximately 5 to 8. The exact pH depends on the exact conditions of the water source; for example, water that comes in contact with minerals and water from rain or springs have different pH.$^{1,2}$ Accordingly, a neutral pH is appropriate to use when studying environmental systems. For these studies, pH 5.5 was selected because it was within the natural groundwater pH range but was still acidic enough to avoid any potential of hydrolysis of Sr and Y.

A standard method for the characterization of an element’s interaction with a naturally occurring molecule, such as humic acid (HA), is via competitive solvent extraction, as mentioned in Appendix E. In order to complete this characterization, a functional solvent extraction system is required. These studies sought to characterize the efficacy of solvent extraction systems at pH 5.5 to determine what extractant system would be ideal for studying the Sr and/or Y.
Three commonly used extractants were selected, di-(2-ethylhexyl)phosphoric acid (HDEHP), 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (HEHEHP), and 2-thenoyltrifluoroacetone (TTA); their respective structures are shown in Figure C.1. The behavior of these three extractants is well characterized for the extraction of trivalent metal ions at acidic conditions.\textsuperscript{3-6} However, few studies have evaluated their extraction abilities at near neutral pH. This present work sought to determine if a solvent extraction system for Sr or Y under non-acidic conditions was feasible using these available organic extractants.

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{structures.png}
\caption{Structures of di-(2-ethylhexyl)phosphoric acid (A), 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (B), and 2-thenoyltrifluoroacetone (C)}
\end{figure}

\textbf{Experimental}

\textit{Instrumentation}

Stable isotopes of Sr and Y were quantified via ICP-OES using an Agilent 5100 SVDV ICP-OES with an SPS 3 autosampler with a 1.3 mm interior diameter inert PTFE sleeved probe, using a computer running ICP Expert Version 7.1.0.6821 (Agilent Technologies, Santa Clara, CA). The exact instrument run conditions for both aqueous and organic sample analysis are detailed in Table C.1. Samples were diluted with 2\% HNO\textsubscript{3} or 10\textsuperscript{-2} M HDEHP in dodecane for aqueous and organic solutions respectively prior to analysis.
<table>
<thead>
<tr>
<th>Instrumental Operating Conditions</th>
<th>Aqueous Solutions</th>
<th>Organic Solutions</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Torch</strong></td>
<td>1.8 mm injector, one piece Torch Agilent G8010-60228</td>
<td>1.4 mm injector, demountable Torch Agilent G8010-60233</td>
</tr>
<tr>
<td><strong>Spray Chamber</strong></td>
<td>Twister Spray Chamber with helix, Glass Expansion 20-809-9199HE</td>
<td></td>
</tr>
<tr>
<td><strong>Nebulizer</strong></td>
<td>SeaSpray 2mL/min Glass Expansion A14-07-USS2</td>
<td>Conikal 2mL/min Glass Expansion A14-07-UC2</td>
</tr>
<tr>
<td><strong>Pump Tubing Material</strong></td>
<td>PVC</td>
<td>Solva Flex</td>
</tr>
<tr>
<td><strong>Sample Pump Speed (rpm)</strong></td>
<td>12</td>
<td>12</td>
</tr>
<tr>
<td><strong>Uptake Delay (s)</strong></td>
<td>25</td>
<td>30</td>
</tr>
<tr>
<td><strong>Rinse Time (s)</strong></td>
<td>30</td>
<td>40</td>
</tr>
<tr>
<td><strong>Read Time (s)</strong></td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td><strong>RF Power (kW)</strong></td>
<td>1.20</td>
<td>1.20</td>
</tr>
<tr>
<td><strong>Stabilization Time (s)</strong></td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td><strong>Viewing Mode</strong></td>
<td>SVDV*</td>
<td>SVDV*</td>
</tr>
<tr>
<td><strong>Viewing Height (mm)</strong></td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td><strong>Nebulizer Flow (L/min)</strong></td>
<td>0.7</td>
<td>0.7</td>
</tr>
<tr>
<td><strong>Plasma Flow (L/min)</strong></td>
<td>13</td>
<td>12</td>
</tr>
<tr>
<td><strong>Aux Flow (L/min)</strong></td>
<td>0</td>
<td>1</td>
</tr>
</tbody>
</table>

*SVDV: Synchronous Vertical Dual View*
Radioactive isotopes of Sr and Y were quantified via LSC with Ecoscint Original (National Diagnostic, Atlanta, GA) on a Beckman LS 6500 scintillation counter (Beckman Coulter, Brea, CA). The counting window was set for all channels to be open and count times were 5 or 20 minutes, dependent on the activity of the sample.

Reagents

Reagent grade chemicals were obtained from Sigma Aldrich (St. Louis, MO), JT Baker (Center Valley, PA), Thermo Fisher (Waltham, MA), and Alfa Aesar (Ward Hill, MA). Single element aqueous phase ICP standards were purchased from Inorganic Ventures (Christiansburg, VA) and prepared as multi-element cocktails in 2% HNO₃ via gravimetric serial dilutions. Single element organic phase ICP standards were purchased from VHG Labs (Manchester, NH) and prepared as multi-element cocktails via gravimetric serial dilution in 10⁻² M HDEHP in dodecane. Strontium-90 radiotracer was purchased through the National Isotope Development Center (Oak Ridge, TN) and was sourced from Pacific Northwest National Laboratory (Richland, WA). HDEHP, HEHEHP, and TTA were purified prior to use; the purifications are detailed in Appendix B. All other reagents were used without purification.

Distribution Studies

The generalized reaction that occurs during solvent extraction can be expressed with the following equilibrium (C.1) where M is the metal ion of interest, L is the organic complexant, and ML is the metal-ligand complex in the organic phase.

\[
M_{\text{aq}}^{n+} + L_{\text{org}}^{h-} \rightleftharpoons ML_{\text{org}}^{n-h}
\]

This equation simplifies the system with the assumptions that the metal is the only cation that is extracted into the aqueous phase and that the supporting electrolyte and buffer ions do not interact with the system. In this simplified system consisting of an organic complexant and a metal in the aqueous phase, in which
the complexant brings the metal into the organic phase, the distribution ratio can be calculated using Equation C.2.

\[
D = \frac{\sum [M]_{(org)}}{\sum [M]_{(aq)}}
\]

C.2

In these studies, D was determined using one of two different techniques; 1) by directly measuring both the aqueous and organic phases, either with ICP-OES for stable samples or LSC for radiotracers or 2) by only measuring the aqueous phase with ICP-OES and then determining the concentration of the organic phase using Equation C.3; where the initial concentration, \([M]_{(aq)}^0\), is the concentration of the aqueous phase sample that has not been contacted with an organic phase.

\[
[M]_{(org)} = [M]_{(aq)}^0 - [M]_{(aq)}
\]

C.3

The inherent error in technique 2 for determining D values is higher due to the fact that third phase formation and/or loss due to element sorption on the vial cannot be accounted for. However, this technique is appealing because of decreased analysis time and decreased waste. Each study covered in the results and discussion section notes which technique was used for determining the D values.

In these studies, \(10^{-5}\) M Sr and \(10^{-5}\) M Y were used as the metal analytes; for the radioactive studies, a spike of \(^{90}\text{Sr}^{90}\text{Y}\) in 1% HClO\(_4\) was added to bring the activity up to the desired level. The aqueous phase was buffered at pH values ranging from 4 to 5.5; 1 mM MES hydrate was used for 5.5 and the rest of the studies were conducted using 10 mM acetate buffer. An ionic strength of 0.1 was maintained with the addition of anhydrous NaClO\(_4\). The organic phase consisted of different solvents with one of three different extractants: HDEHP, HEHEHP, and TTA.

Solvent extraction studies were conducted by contacting 2 mL of aqueous phase with 2 mL of organic phase in glass vials at 25°C in triplicate. Mixing was conducted using an orbital shaker (Barnstead Multi-purpose rotator, Barnstead International, Dubuque, IA) or a vortex mixer (Fisher Scientific, Hampton, NH). The specific contact details for each study are noted in the results discussion.
Bateman Derived Counting Technique

The LSC counting technique used to determine the activities of $^{90}$Sr and $^{90}$Y in each of the spiked solutions is detailed in Chapter 4 and Appendix D

Results and Discussion

HDEHP

Unpurified HDEHP was diluted in dodecane and ranged in concentrations from $10^{-7}$ to $10^{-3}$ M. Aqueous solutions of $10^{-7}$ M Sr or Y in 0.1 M NaClO$_4$ buffered at pH 5.5 with 1 mM MES hydrate were prepared. Solvent extraction samples consisted of 5 mL of each phase that were contacted for 60 minutes on a rotary mixer. In the study, the distribution coefficients, $D$, were determined by only using the concentrations of the metals in the aqueous phase and back calculating the organic phase concentrations from the initial metal concentrations. The results from the study are presented with Figure C.2. As expected, Sr is not extracted by HDEHP under non-basic conditions.$^{7-9}$ Yttrium extraction reached its maximum for HDEHP concentration of $4\cdot10^{-6}$ M.
The study of Sr extraction by HDEHP was continued; Y extraction by HDEHP was further investigated. Five mL of $10^{-7}$ M Y in 0.1 M NaClO$_4$ with pH buffered at 5.5 with 1 mM MES hydrate was contacted with 5 mL of varying concentrations of HDEHP in dodecane for 60 minutes. To ensure mixing efficiency, one sample set was mixed on a rotary mixer and another on an orbital shaker. Figure C.3 shows the results of this study. Both mixing techniques allowed for the systems to reach equilibrium but under these conditions the formation of DEHP containing micelles is likely.

**Figure C.2.** Distribution ratios of the extraction of $10^{-7}$ M Sr and $10^{-7}$ M Y in 0.1 M NaClO$_4$ with pH buffered at 5.5 with 1 mM MES hydrate contacting varied concentrations of HDEHP ($10^{-7} – 10^{-3}$ M) in dodecane for 60 minutes on a rotary mixer.
Figure C.3. Distribution ratios for the extraction of $10^{-7}$ M Y with HDEHP in dodecane using two different mixing types.

The lack of linearity in the higher HDEHP concentrations can be explained by the formation of HDEHP micelles, with the size depending on the mixing type. Aqueous solution at pH 5.5 may too basic for HDEHP to function properly; the literature reports issues using HDEHP at higher pH than 3.6, corresponding to HDEHP’s pK$_a$ value of approximately 3.$^{10,11}$ At pH 5.5, one possibility is the DEHP$^-$ ion is forming NaDEHP(HDEHP)$_3$ with the Na$^+$ from the supporting electrolyte.$^{12}$ When the concentration of HDEHP was increased to 0.1 M HDEHP, a third phase was readily. After centrifugation, the third phase was apparent as cloudiness in the aqueous phase and as a layer on the surface of the vials.

HEHEHEHP
In order to avoid third phase formation, HEHEHP was selected over HDEHP with the theory that the increased pKₐ of 3.30 would decrease the likelihood of a third phase forming compared to HDEHP. A sample of 3 mL of 10⁻⁵ M Y in 0.1 M NaClO₄ buffered at pH 5.5 with 1 mM MES hydrate was contacted with 3 mL of varying concentrations of HEHEHP in dodecane for 2 hours on an orbital shaker. The aqueous phase was analyzed with an internal standard of Ca added to remove any error due to instrumental (ICP-OES) drift.

![Figure C.4](image)

**Figure C.4.** Distribution ratios for 10⁻⁵ M Y contacting varied concentrations of HEHEHP in dodecane, 1σ errors calculated via triplicate.

The distribution values are shown in Figure C.4, the associated errors were deemed too large. Since an internal standard was added during the dilution prior to ICP-OES analysis, instrumental error can be assumed to be a nonissue and the experiment has to be refined. To gain a more complete understanding
of the system, an experiment using radiotracer and LSC was performed, to allow both phases to be measured; such an experiment does not require sample dilution.

A solution of $10^{-5}$ M Sr and $10^{-5}$ M Y and 0.1 M NaClO$_4$ buffered at pH 5.5 with 1 mM MES hydrate was spiked with an aliquot of $^{90}$Sr in 1% HClO$_4$ (the radiotracer had sufficient time to reach equilibrium and $^{90}$Sr and $^{90}$Y are in secular equilibrium). After allowing the spiked solution to equilibrate for an hour, the pH was brought back up to a value of 5.5. A volume of 2 mL of the spiked solution was contacted with 2 mL of $10^{-2}$ M HEHEHP in dodecane for 2 hours on an orbital shaker. After contact, 1 mL aliquots of both phases and the initial aqueous phase were analyzed via LSC with a count time of 20 minutes. The initial counts are detailed in Table C.2.

**Table C.2.** Count data for $10^{-5}$ M Sr, $10^{-5}$ M Y contacting $10^{-2}$ M HEHEHP in dodecane.

<table>
<thead>
<tr>
<th></th>
<th>Aqueous (Bq)</th>
<th>Organic (Bq)</th>
<th>Total (Bq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Replicate 1</td>
<td>153</td>
<td>12.3</td>
<td>165.3</td>
</tr>
<tr>
<td>Replicate 2</td>
<td>163</td>
<td>17.8</td>
<td>180.8</td>
</tr>
<tr>
<td>Replicate 3</td>
<td>158</td>
<td>14.1</td>
<td>172.1</td>
</tr>
<tr>
<td>Replicate 4</td>
<td>172</td>
<td>14.0</td>
<td>186</td>
</tr>
<tr>
<td>Uncontacted</td>
<td>255</td>
<td>-</td>
<td>255</td>
</tr>
</tbody>
</table>

The total activities are 4,000-5,000 cpm lower than the uncontacted aqueous aliquot, for all the replicates. The most likely cause of this is third phase formation still occurring. The individual activities for $^{90}$Sr and $^{90}$Y were determined using the Bateman derived counting technique detailed in Chapter 4. The curve fitting data for each of the 4 replicates and the uncontacted aqueous phase are listed in
Table C.3. Using these x-values, the initial activities of $^{90}\text{Sr}$ and $^{90}\text{Y}$ were determined (Table C.4).

Strontium is negligibly extracted, which is expected for a divalent ion with HEHEHP. However, more than 50 percent of the Y is not accounted for by two phases (aqueous/organic). With this information, it is evident that there is still third phase formation despite the switch to HEHEHP.

Table C.3. Non-linear curve fit data with the Bateman derived function for $10^{-5}$ M Sr and $10^{-5}$ M Y contacting $10^{-2}$ M HEHEHP in dodecane.

<table>
<thead>
<tr>
<th>Sample</th>
<th>x-Value</th>
<th>Standard Error</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 – Organic</td>
<td>0.304</td>
<td>0.001</td>
<td>0.99011</td>
</tr>
<tr>
<td>1 – Aqueous</td>
<td>0.8381</td>
<td>0.0004</td>
<td>0.99968</td>
</tr>
<tr>
<td>2 – Organic</td>
<td>0.2816</td>
<td>0.0009</td>
<td>0.99673</td>
</tr>
<tr>
<td>2 – Aqueous</td>
<td>0.8380</td>
<td>0.0004</td>
<td>0.99967</td>
</tr>
<tr>
<td>3 – Organic</td>
<td>0.2382</td>
<td>0.0007</td>
<td>0.99846</td>
</tr>
<tr>
<td>3 – Aqueous</td>
<td>0.8275</td>
<td>0.0008</td>
<td>0.99882</td>
</tr>
<tr>
<td>4 - Organic</td>
<td>0.2662</td>
<td>0.0007</td>
<td>0.99813</td>
</tr>
<tr>
<td>4 – Aqueous</td>
<td>0.7984</td>
<td>0.0004</td>
<td>0.99972</td>
</tr>
<tr>
<td>Uncontacted</td>
<td>0.5423</td>
<td>0.0002</td>
<td>0.99671</td>
</tr>
</tbody>
</table>
Table C.4. Initial $^{90}\text{Sr}$ and $^{90}\text{Y}$ activities following contact of a spiked $10^{-5}$ M Sr and $10^{-5}$ M Y aqueous phase with $10^{-2}$ M HEHEHP.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$^{90}\text{Sr}$ (Bq)</th>
<th>$^{90}\text{Y}$ (Bq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncontacted</td>
<td>138</td>
<td>117</td>
</tr>
<tr>
<td>1 – Organic</td>
<td>3.76</td>
<td>8.53</td>
</tr>
<tr>
<td>1 – Aqueous</td>
<td>128</td>
<td>24.7</td>
</tr>
<tr>
<td>1 – Total</td>
<td>132</td>
<td>33.2</td>
</tr>
<tr>
<td>2 – Organic</td>
<td>3.60</td>
<td>9.16</td>
</tr>
<tr>
<td>2 – Aqueous</td>
<td>137</td>
<td>26.0</td>
</tr>
<tr>
<td>2 – Total</td>
<td>141</td>
<td>35.2</td>
</tr>
<tr>
<td>3 – Organic</td>
<td>3.36</td>
<td>10.7</td>
</tr>
<tr>
<td>3 – Aqueous</td>
<td>130</td>
<td>27.9</td>
</tr>
<tr>
<td>3 – Total</td>
<td>133</td>
<td>38.6</td>
</tr>
<tr>
<td>4 – Organic</td>
<td>3.68</td>
<td>10.3</td>
</tr>
<tr>
<td>4 – Aqueous</td>
<td>138</td>
<td>34.6</td>
</tr>
<tr>
<td>4 – Total</td>
<td>142</td>
<td>44.9</td>
</tr>
</tbody>
</table>

Another set of experiments was prepared with the extractant HEHEHP; the organic diluent was switched to kerosene. The hypothesis is that the additional surfactants and smaller organic molecules will increase the organic solubility of the Y-HEHEHP third phase. Additionally, one sample set was prepared with pH 5.5 and another with pH 5; a decreased pH could decrease the third phase. Solutions of $10^{-5}$ M Sr and $10^{-5}$ M Y with 0.1 M NaClO$_4$ were spiked with the $^{90}\text{Sr}$ radiotracer and the pH was then adjusted to pH 5 or 5.5. A volume of 2 mL of the solution was contacted with 2 mL of $10^{-2}$ M HEHEHP in kerosene for 2 h on an orbital shaker. After contacting, the solutions were centrifuged and the counts of 1 mL aliquots were measured with LSC. The total activities of each isotope from both phases are shown in Table C.5.
Again a large portion of the $^{90}$Y is not accounted for in the aqueous and organic phases. It is evident the issue lies with the organic extractant system; there is a solubility issue with the Y-HEHEHP complex, even at pH 5. This is likely due to the pH being too high for HEHEHP; which has a pK$_a$ of 3.3 and will behave similar to HDEHP in this pH range.

**Table C.5.** pH dependent study for $10^{-5}$ M Sr and $10^{-5}$ M Y contacting $10^{-2}$ M HEHEHP in kerosene, the values shown are the total of the activities measured in both phases.

<table>
<thead>
<tr>
<th></th>
<th>Total $^{90}$Sr (Bq)</th>
<th>Total $^{90}$Y (Bq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 5 Stock</td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH 5 – Replicate 1</td>
<td>131</td>
<td>30.6</td>
</tr>
<tr>
<td>pH 5 – Replicate 2</td>
<td>155</td>
<td>59.8</td>
</tr>
<tr>
<td>pH 5 – Replicate 3</td>
<td>120</td>
<td>23.2</td>
</tr>
<tr>
<td>pH 5.5 Stock</td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH 5.5 – Replicate 1</td>
<td>136</td>
<td>35.2</td>
</tr>
<tr>
<td>pH 5.5 – Replicate 2</td>
<td>131</td>
<td>49.0</td>
</tr>
<tr>
<td>pH 5.5 – Replicate 3</td>
<td>124</td>
<td>36.6</td>
</tr>
</tbody>
</table>

One final study was conducted with HEHEHP in order to determine if a change of diluent eradicates the third phase formation. For this study, the aqueous phase consisted of the spiked $10^{-5}$ M Sr and $10^{-5}$ M Y with 0.1 M NaClO$_4$, buffered at pH 5.5 with 1 mM MES hydrate. A volume of 2 mL of this solution was contacted with 2 mL of 0.05 M HEHEHP in a 1% octanol in dodecane solution. Octanol is traditionally used as phase modifier and chosen in hopes that it increases the Y-HEHEHP complex solubility in the organic phase; samples were run in duplicates. Only 30% of the $^{90}$Y was accounted for in the aqueous and organic samples. At pH 5 or above, HEHEHP is effective at extracting Y, but a fraction of Y is
present in a third phase, either at the interface or (more likely based on visual observation of the sample vials) on the surface of the vial.

TTA

TTA has been used in extractions from highly acidic to basic conditions. TTA extracts divalent metal ions at basic pH, while TTA is a well characterized complexant for trivalent and tetravalent metal ions in solutions below pH 4.

The first contact study was a simple proof of concept to investigate the capability of TTA to extract Sr and Y. A solution of $10^{-5}$ M Sr and $10^{-5}$ M Y with 300 Bq/mL $^{90}$Sr/$^{90}$Y in 0.1 M NaClO$_4$ buffered at pH 5.5 with 1 mM MES was contacted with 0.05 M TTA in dodecane for 2 hours on the orbital shaker. This contact resulted with a loss of just over 10 percent of the total activity for both isotopes. The loss can be due to sorption on the vial and cap and does not necessarily signify the formation of a third phase.

A brief concentration dependence study was conducted with a solution of $10^{-5}$ M Sr, $10^{-5}$ M Y with 250 Bq/mL $^{90}$Sr/$^{90}$Y in 0.1 M NaClO$_4$ buffered at pH 5.5 with 1 mM MES was contacted with TTA ($10^{-3}$ to $5\cdot10^{-2}$ M) in dodecane for 2 hours on an orbital shaker. Relatively consistent D values were obtained for each set of replicates, however, the percentage of missing $^{90}$Y increased as the concentration of TTA increased. This could be due to the sources of loss mentioned earlier: sorption or the formation of a third phase. The fact that the organic phase contains TTA and is being quantified via LSC introduces a new potential problem.

The structure of TTA is shown in Figure C.5; the point of interest is the 2 double bonds in the ring structure. The $\pi$ electrons present in these double bonds can cause chemical quenching. Chemical quenching occurs when components other than the scintillation cocktails absorb the decay energy, leading
to a decrease in the amount of light produced via the scintillation process and a decrease in measured activity.

![Structure of 2-thenoyl trifluoroacetone (TTA)](image)

**Figure C.5.** Structure of 2-thenoyl trifluoroacetone (TTA)

In order to quantify the quenching effect of TTA, a contact study was performed in triplicate; 2 mL of a spiked $10^{-5}$ M Sr, $10^{-5}$ M Y in 0.1 M NaClO$_4$ buffered at pH 5.5 with 1 mM MES was contacted with 2 mL of 0.02 M TTA in dodecane on an orbital shaker for 2 hours. The samples were then centrifuged to ensure complete phase separation. Aliquots of the organic phase (0.5 mL) were added to 2 mL of Ecoscint Original, and counted with LSC for 5 min. After this first LSC counting, additional LSC cocktail was added to each sample and the samples were re-counted. This process was repeated until a total of 20 mL of Ecoscint Original had been added to each sample. The results of this experiment are presented in Figure C.6. As the volume of scintillation fluid added is increased, the relative concentration of TTA decreases. If chemical quenching were occurring, the measured activity would increase as the relative TTA concentration decreases. Since all of the measured activities are within error of each other, we conclude that TTA does not produce quenching at these concentrations.
Figure C.6. Measured activity (triplicate samples, 2σ error) of a 0.5 mL aliquot of 0.02 M TTA in dodecane organic phase after contacting a $10^{-5}$ M Sr, $10^{-5}$ M Y with 150 Bq/mL $^{90}$Sr/$^{90}$Y; increasing volumes of Ecoscint Original was added to each sample.

Since quenching is not the source of the discrepancies in the Y concentrations, the assumption was made that we are still encountering a third phase formation. One potential source of the third phase is the organic diluent; TTA is typically diluted in aromatic solvents; dodecane was used in these studies because it had been the diluent used with the HDEHP and HEHEHP studies. A set of contact studies was performed with stable $10^{-5}$ M Sr, $10^{-5}$ M Y in 0.1 M NaClO$_4$ buffered at pH 5.5 with 1 mM MES contacting 0.02 and 0.1 M TTA in three different solvents (xylene, kerosene, and octanes) for 2 hours on an orbital shaker. Octanes and kerosene were selected for their low volatility and the theory that the shorter chain lengths would be more effective at keeping the metal : HEHEHP complex in solution. Aqueous and organic phases were analyzed using ICP-OES (radioisotopes and LSC counting were
eliminated because of potential variation of counting efficiency between the different solvents). With all three solvents, a significant portion of the Y was lost; xylenes was the most effective solvent but still lost approximately thirty percent of the Y, while kerosene lost around forty percent and octanes lost sixty percent. Four different solvents have the same issue, albeit at slightly different magnitudes, so the diluent is not the source of the third phase. The last option is pH: the solubility of TTA in water increases with pH above pH 5.16

Solutions of $10^{-5}$ M Sr and $10^{-5}$ M Y in 0.1 M NaClO$_4$ with 0.01 M acetate buffer was prepared at pH 4.5, 4.25 and 4.0. Volumes of 2 mL aliquot of these solutions were contacted with 0.04 M TTA in xylenes for 2 hours on the orbital shaker. After contacting, the aqueous and organic phases were analyzed using ICP-OES. The results of these studies are shown in Table C.6. All 3 pH points have much less element loss than all of the studies conducted at pH 5.5. Two further trends can be noticed as well: as pH decreases the D value for Y decreases and as pH decreases, the percentage of Y lost decreases.

**Table C.6.** pH dependent study for $10^{-5}$ M Sr and $10^{-5}$ M Y contacting 0.04 M TTA in xylenes, errors shown are $2\sigma$.

<table>
<thead>
<tr>
<th>pH</th>
<th>D (Y)</th>
<th>% Y missing</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.02</td>
<td>1.1 ± 0.2</td>
<td>13.7 ± 0.4</td>
</tr>
<tr>
<td>4.23</td>
<td>3.90 ± 0.09</td>
<td>17.7 ± 0.6</td>
</tr>
<tr>
<td>4.54</td>
<td>16 ± 3</td>
<td>20.4 ± 0.5</td>
</tr>
</tbody>
</table>

**Equilibrium Constant Determination**

With a working solvent extraction system below pH 4.5, the equilibrium constant was determined by varying the concentration of TTA while maintaining a constant pH. $10^{-5}$ M Sr and $10^{-5}$ M Y in 0.9 M NaClO$_4$ and 0.01 M acetate buffer at pH 3.97 was contacted with TTA in xylenes for 2 hours on the
orbital shaker. The TTA concentrations ranged from 0.02 to 0.25 M. After contact, both phases were analyzed via ICP-OES. Using the measured concentrations, the TTA concentrations, and the pH, the equilibrium constant can be determined using Equation C.4.

\[ \log D = \log K_{ex} \frac{[H^+]^3}{[HTTA]^3} \]  

C.4

Which can be simplified to Equation C.5.

\[ \log D = 3 \cdot \log [HTTA] + \log K_{ex} - 3 \cdot \log [H^+] \]  

C.5

To confirm that 3 hydrogens are exchanged, a quick pH dependence study was conducted, contacting the same aqueous solution (adjusted to pH 3.97 and 3.86) with 0.2 M TTA in xylenes. This resulted in the pH dependence plot shown in Figure C.7. The pH dependence had a slope of negative 3, confirming that 3 hydrogens are exchanged.
Figure C.7. The log scale plot of hydronium versus D values for $10^{-5}$ M Y contacting 0.2 M TTA in xylenes.

The D values are determined using the ICP-OES data and then plotted versus the concentration of TTA, shown in Figure C.8.
Figure C.8. The log scale plot of TTA concentration versus D value at pH 3.97 and 3.86, with a linear fit applied to each data set. Errors are $2\sigma$ from triplicates.

Equation C.5 can be used to describe the linear trend lines shown in Figure C.8. Since the system is above acidic conditions, the slope is not the ideal 3 that a trivalent metal typically exhibits with TTA, which corresponds to data shown in the literature.$^9$ Due to this, the 3 in C.5, can be replaced with an n, which is the slope of the plot log D is the y-value of the line, log [HTTA] is the x-value, and lastly, log $K_{ex} = n \cdot \log [H^+]$ is the y-intercept. Using the calculated y-intercepts from the plot, the log $K_{ex}$ can be calculated for each pH using Equation C.6.

$$\log K_{ex} = (Y \text{ intercept}) + (\text{slope}) \cdot \log H^+$$  \hspace{1cm} C.6

This gives the following values for log $K_{ex}$ 13.6$\pm$0.2 for pH 3.97.
Conclusion

Using ICP-OES for analysis of both organic and aqueous solutions and LSC with the Bateman derived curve fitting allowed for both phases to be analyzed for both stable and radiotracer systems. This gave the advantage of being able to switch between the two quantification methods in order to eliminate the analytical technique as the cause of the errors (i.e. quenching with LSC). At pH 5.5, TTA, HEHEHP, and TTA all appear to have issues with the solubility of the ligand complexes being formed. Yttrium was extracted from the aqueous phase in all three systems but it did not remain fully dissolved in the organic phase. In order to avoid third phase formation, the only viable solution is to perform the studies at a lower pH. The upper functional pH limit for TTA appears to be somewhere around 4 - 4.5, which agrees with the literature. The $k_{ex}$ for Sr and Y are determined under these conditions in Chapter 3.
References


APPENDIX D
CURVE FITTING WITH THE BATEMAN DERIVATION

The curve fitting with the Bateman derived function requires a minimum of 2 counts, preferably at least 24 hours apart. After counting, the LSC data needs to be converted to Bq and then normalized so that the initial activity for each sample is 1. The time for each data point needs to be in seconds since the first count (i.e. point number 1 would have \( t = 0 \) s and if point 2 was measured 24 hours later, it would have \( t = 86,400 \) s). This data is then imported into OriginPro, with time as x and the normalized activity as y.

To input the Bateman derived function as a nonlinear curve fitting equation, we open the nonlinear curve fit dialog option (Figure D.1).

![Figure D.1. Nonlinear curve fitting analysis option menus.](image-url)
This provides the dialog box shown in Figure D.2. In this menu, we select <New> from the Category drop down list.

![Dialog box](image)

**Figure D.2.** Nonlinear curve fitting dialog box.
This brings up a new menu to input a name, description and function type (Figure D.3). We type in the desired name and description, select the Explicit model option and Expression as Function Type, and click the next button.

![Function Builder Name and Type](image)

**Figure D.3.** Function builder name and type menu.

The next menu allows for the input of the variables and constants (Figure D.4). For the Bateman derivation fitting, there is the independent variable (time), dependent variable (measured normalized activity), and parameter (A_{Sr}/A_{tot} ratio), and 3 constants (initial activity, \(\lambda_{Sr}, \lambda_Y\)). The measured activities are normalized in order to allow for multiple sample sets to be processed simultaneously without requiring the initial activity constant to be changed.
Figure D.4. Constants and variables menu

Clicking next brings up the menu to input the values for the constants and the expression (Figure D.5). Initial Activity (A0) has a value of 1, and L1 and L2 are the decay coefficients for $^{90}\text{Sr}$ and $^{90}\text{Y}$ in s$^{-1}$. The expression is the Bateman derived equation detailed in Chapter 4, the exact format used in this menu is shown in Equation D.1.

$$x*A0*\exp(-L1*t)+((x*A0)/(L2-L1))*(\exp(-L1*t)-\exp(-L2*t))*L2+(1-x)*A0*\exp(-L2*t) \quad \text{D.1}$$
Figure D.5. Menu for inputting the expression and constant values

The next menu brings up the boundary options for $x$ (Figure D.6). Since $x$ is a ratio, its minimum is 0 and its maximum is 1.
Figure D.6. Boundary options for calculating \( x (A_{Sf}/A_{in}) \)

The fitting can then be applied to a set of \( x \) and \( y \) data in OriginPro. In this example, the activities were not normalized. In order to compensate for this, the initial activity had to be changed to first measured activity instead of the value of 1 discussed previously. Doing so yields the following data:
Table D.1. Nonlinear curve fit report “Notes.”

<table>
<thead>
<tr>
<th>Description</th>
<th>Nonlinear Curve Fit</th>
</tr>
</thead>
<tbody>
<tr>
<td>User Name</td>
<td>kevin.swearingen</td>
</tr>
<tr>
<td>Operation Time</td>
<td>1/6/2017 10:14:31</td>
</tr>
<tr>
<td>Iteration Algorithm</td>
<td>Levenberg Marquardt</td>
</tr>
<tr>
<td>Model</td>
<td>BatemanFitting (User)</td>
</tr>
<tr>
<td>Number of Parameters</td>
<td>1</td>
</tr>
<tr>
<td>Number of Derived Parameters</td>
<td>0</td>
</tr>
<tr>
<td>Number of Datasets</td>
<td>1</td>
</tr>
<tr>
<td>Equation</td>
<td>x<em>A0</em>exp(-L1<em>t)+((x</em>A0)/(L2-L1))<em>(exp(-L1</em>t)-exp(-L2*t))<em>L2+(1-x)<em>A0</em>exp(-L2</em>t)</td>
</tr>
<tr>
<td>Report Status</td>
<td>New Analysis Report</td>
</tr>
</tbody>
</table>

Special Input Handling

Data Filter | No |

Table D.2. Input data for the nonlinear curve fit

<table>
<thead>
<tr>
<th>Dep/Indep</th>
<th>Data</th>
<th>Range</th>
<th>Weight Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activity</td>
<td>B Dep</td>
<td>[Book1]Sheet1!B&quot;Activity&quot;</td>
<td>[1*:21*]</td>
</tr>
<tr>
<td>t</td>
<td>Indep</td>
<td>[Book1]Sheet1!A&quot;Time&quot;</td>
<td>[1*:21*]</td>
</tr>
</tbody>
</table>
Table D.3. Nonlinear curve fit function parameters.

<table>
<thead>
<tr>
<th>Value</th>
<th>Standard Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activity X</td>
<td>0.54233</td>
</tr>
<tr>
<td></td>
<td>1.77927E-4</td>
</tr>
</tbody>
</table>

Reduced Chi-sqr = 0.122476683702

COD(R^2) = 0.99671263673049

Iterations Performed = 4

Total Iterations in Session = 4

Fit converged. Chi-Sqr tolerance value of 1E-9 was reached.

Constants : A0=255.00083 L1=7.63179e-010 L2=3.0047e-006

Table D.4. Nonlinear curve fit report statistics.

<table>
<thead>
<tr>
<th>Activity</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of Points</td>
<td>21</td>
</tr>
<tr>
<td>Degrees of Freedom</td>
<td>20</td>
</tr>
<tr>
<td>Reduced Chi-Sqr</td>
<td>0.12248</td>
</tr>
<tr>
<td>Residual Sum of Squares</td>
<td>2.44953</td>
</tr>
<tr>
<td>Adj. R-Square</td>
<td>0.99671</td>
</tr>
<tr>
<td>Fit Status</td>
<td>Succeeded(100)</td>
</tr>
</tbody>
</table>

Fit Status Code : 100 : Fit converged. Chi-Sqr tolerance value of 1E-9 was reached.
### Table D.5. Nonlinear curve fit report summary

<table>
<thead>
<tr>
<th>Value</th>
<th>Std Error</th>
<th>Reduced Chi-Sqr</th>
<th>Adj R-Square</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activity</td>
<td>0.54233</td>
<td>1.77927E-4</td>
<td>0.12248</td>
</tr>
</tbody>
</table>

### Table D.6. Nonlinear curve fit report ANOVA.

<table>
<thead>
<tr>
<th>DF Type</th>
<th>DF</th>
<th>Sum of Squares</th>
<th>Mean Square</th>
<th>F Value</th>
<th>Prob&gt;F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activity</td>
<td></td>
<td>1.5543E6</td>
<td>1.5543E6</td>
<td>1.26906E7</td>
<td>1</td>
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<tr>
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<td>20</td>
<td>2.44953</td>
<td>0.12248</td>
<td></td>
</tr>
<tr>
<td>Activity</td>
<td></td>
<td>21</td>
<td>1.5543E6</td>
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</tr>
<tr>
<td>Activity</td>
<td></td>
<td>20</td>
<td>745.13629</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure D.7. The resulting curve fit from the function. In this case, the activity was not normalized and the initial activity had to be manually input.
Figure D.8. Residual plots for the nonlinear curve fit shown in Figure D.7.
APPENDIX E

INTERACTION OF SR AND Y WITH NATURALLY OCCURRING COLLOIDS

Introduction
Humic acid (HA) is a family of organic acids formed from the decomposition of organisms. As such, there is no specific structure for HA, but rather a few defining characteristics. HA molecules have aromatic rings, carboxylic acid groups, and phenol groups; one hypothetical structure for a single HA molecule is shown in Figure E.1. Due to HA being formed from the decomposition of organism, it is found in many soil and aquatic environmental systems. The carboxylic acid groups present on HA allow it to function as a complexant, binding with metal ions present in the environment.

![HA molecule structure](image)

**Figure E.1.** One hypothetical structure for terrigenous HA.¹

The earth’s crust is composed of approximately 27% Si in various forms. Silica (SiO₂) is found naturally in the environment as quartz and is a major constituent of many types of sand. Accordingly, silica is present in many ground water systems. In some environmental systems, silica is one of the primary...
components; the presence of Si and/or HA can affect the environmental fractionation of Sr and Y following an environmental release of fission products. The metal ions can interact with both the minerals and the mineral surfaces. Literature studies describe the sorption of various elements to a number of different mineral types.\textsuperscript{2-5} Additional studies have shown that the presence of HA can promote or inhibit sorption of metal ions to mineral surfaces.\textsuperscript{6-8}

These studies were done as a brief survey of the interactions of HA and colloidal silica with Sr and Y. Additionally, new techniques were developed to improve the characterization of a HA. By definition, HA is a very complex substance and new characterization techniques will allow for studies to be conducted with more thorough understanding of the HA system.

**Experimental**

**Reagents**

Reagent grade chemicals were obtained from Thermo Fisher Scientific (Waltham, MA, USA) and JT Baker (Center Valley, PA). Solutions were prepared using 18.2 MΩ·cm distilled deionized water (DIW) from a Millipore Synergy Water Purification System (EMD Millipore, Billerica, MA, USA). Single element aqueous phase ICP standards were purchased from Inorganic Ventures (Christiansburg, VA) and prepared via gravimetric serial dilutions in 2% HNO\textsubscript{3}. Elliott Soil and Suwannee River HA were purchased from the International Humic Substance Society (IHSS, St. Paul, MN). The HA was purified according to the procedure discussed in the Methods section and all the other reagents were used without further purification.

**Instrumentation**

Si concentrations were measured via ICP-OES using an Agilent 5100 SVDV ICP-OES with an SPS 3 autosampler with a 1.3 mm interior diameter inert PTFE sleeved probe, using a computer running ICP
Samples were diluted with 2% HNO$_3$ prior to analysis. HA concentrations were determined via UV-Vis absorbance at 254 nm on a Varian Cary 5000 UV/Vis-NIR running Varian UV Scan Version 3.00(339) (Agilent Technologies, Santa Clara, CA). Ultracentrifugation was performed using a Sorvall WX Ultra 80 Series Centrifuge (Thermo Fisher Scientific, Waltham, MA, USA). Centrifugation was performed using a protocol detailed in Table E.1.

**Table E.1.** The protocol used for centrifuging the colloidal silica and removing all particles larger than 8 nm.

<table>
<thead>
<tr>
<th>Speed (rpm)</th>
<th>Time (minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15,000</td>
<td>2</td>
</tr>
<tr>
<td>30,000</td>
<td>2</td>
</tr>
<tr>
<td>45,000</td>
<td>2</td>
</tr>
<tr>
<td>60,000</td>
<td>30</td>
</tr>
</tbody>
</table>

*Humic Acid Purification*

HA was purified by first dissolving Aldrich sodium humate in 10$^{-2}$ M NaOH and filtering through glass wool. After filtration, the HA was precipitated with the addition of sufficient concentrated HCl to bring the pH down to approximately 1. After addition of HCl, the solution was mixed on an orbital mixer to ensure complete precipitation. The precipitated HA was separated via centrifugation and the supernatant was removed. The precipitate was redissolved in 10$^{-2}$ M NaOH and was centrifuged to remove any undissolved particulate. The precipitation and dissolution was repeated 2 more times to ensure the removal of impurities. After 3 cycles, the HA was precipitated with HCl and the supernatant was removed. The HA precipitate was dried using a FreeZone 1 Liter Benchtop Freeze Drier (Labconco,
Kansas City, MO). After purification, the HA’s purity was measured via ashing and Total Reflection X-ray Fluorescence (TXRF).

Ashing was performed using a Perkin Elmer Pyris 1 TGA (Waltham, MA); the samples were heated to 500°C at 10°C per minute and then held at 500°C for 5 hours. To provide a means of comparison, Elliott HA from the International Humic Substance Society (IHSS), which has been homogenized and characterized by the IHSS was ashed using the same protocol.

Due to the complex nature of HA and the fact that it precipitates under acidic conditions, metal impurities are not typically quantified beyond ashing. Anything that is not ashed is assumed to be a metal impurity. In the majority of studies, no further analysis is performed to determine the identity of the metal impurities. Purified Aldrich HA and IHSS Elliott Soil and Suwannee River HA were analyzed via Total Reflection X-ray Fluorescence (TXRF) (Bruker S2 Picofox, Billerica, MA) to evaluate its efficacy at quantifying metal impurities in HA.

Ultracentrifugation

A modified version of Stokes Law (Equation E.1) was used to determine the time and rotational speed required to remove the colloidal silica from the slurries.

\[ D = \frac{18 \cdot \eta \cdot \ln \left( \frac{R_f}{R_0} \right)}{\left( \rho_p - \rho_s \right) \cdot \omega^2 \cdot t} \quad \text{E.1} \]

Where D is the particle diameter (cm), \( \eta \) is the viscosity of the solvent (poise, g·cm⁻¹·s⁻¹), \( R_f \) is the final radius of rotation (cm), \( R_0 \) is the initial radius of rotation (cm), \( \rho_p \) is the density of the particle (g·cm⁻³), \( \rho_s \) is the density of the solvent (g·cm⁻³), \( \omega \) is the rotational velocity (rad/s), and \( t \) is the time in seconds. For these studies, two assumptions were made. 1) The density of the colloidal silica particles was 2.196 g·cm⁻³ (the density of amorphous silica). 2) The density and viscosity of the 0.1 M NaClO₄
solution was the same as water at 25°C (0.0089 g·cm⁻¹·s⁻¹ and 0.997 g·cm⁻³). With a rotational speed of 60,000 rpm (6,283 rad·s⁻¹) and a spin time of 30 minutes, the centrifuge will remove any silica particles larger than 7.9 nm.

_Silica Dissolution_

Samples containing 1,000 ppm colloidal silica (0.02 µm diameter) in 0.1 M NaClO₄ were pH adjusted using HClO₄ or NaOH to provide a pH range from 3.4 to 9.4. Samples were equilibrated for 24 hours on an orbital shaker (Barnstead Multi-purpose rotator, Barnstead International, Dubuque, IA). After equilibration, the samples were centrifuged using the previously described protocol and the supernatant was diluted and analyzed via ICP-OES.

_HA Sorption on Silica_

Samples containing 14 ppm HA in 0.1 M NaClO₄ at pH 6.5 with silica concentrations ranging from 0.1 to 10,000 ppm were mixed for 24 hours on the orbital shaker. After mixing, an aliquot of each sample was centrifuged using the above protocol and the supernatant was measured on the UV-Vis, the absorbance at 254 nm was compared to that of an aliquot of the same solution that had not been centrifuged to determine the percentage of HA that had sorbed to the silica. An overview of the method is presented with Figure E.2.
**Figure E.2.** Flowchart of the method used to determine HA sorption on colloidal silica.

**Humic Acid Stability Constants**

Using the stability constant of TTA with Y determined in Chapter 4, the complexation of Y with HA was examined using solvent extraction. The organic phase consisted of 76 mM TTA in xylenes and was contacted with an aqueous phase composed of 0 to 100 ppm purified HA, $10^{-5}$ M Y, 0.9 M NaClO₄, and buffered at pH 4.1 with 0.01 M acetate buffer. The solutions were contacted for 24 hours on a rotary shaker. After contact, the samples were centrifuged for 5 minutes at 3,000 rpm.

**Results and Discussion**

**Humic Acid Purity Analyses**

HA is typically viewed as being pure when it has an ash percent of less than 10%. The ashing results for three individual runs are shown in Figure E.3. The final ash percent was 26±2% (2σ). These values are higher than the typical ash percents for purified humic acid (<10%). In order to gauge the efficacy of the TGA ashing methods, samples of Elliott Soil humic acid from the IHSS were ashed using the same
technique. The results from a set of triplicates is shown in Figure E.4, the 3 replicates had an average ash percent of 30±10% (2σ), which is much higher than the percentage reported by the IHSS (0.88%).

![Graph showing mass percentage over time for three trials](image)

**Figure E.3.** Three replicate runs of purified Aldrich Humic acid using the TGA ashing method.
Figure E.4. Three replicate runs of IHSS Elliott Soil humic acid using the TGA ashing method.

Though the percentages are significantly higher than typically reported, the increase is not likely only due to impurities in the current lot of Aldrich HA. Since the IHSS reference material had a much higher ash percent than reported, one of the causes is likely the difference in sample handling and ashing process of TGA ashing versus using a traditional furnace and cooling then weighing the sample. With the TGA, there are fewer opportunities for a loss of mass to occur since there are no transfers occurring.

Ashing is the traditional technique used for the determination of impurities in HA. One of the disadvantages of this technique is that it only determines the presence of inorganic impurities without quantifying what they are. The efficacy of TXRF for the quantification of the inorganic impurities in HA was examined. Figure E.5 presents the spectra for both purified and unpurified Aldrich HA. The blue labels are the elements that are present due to the instrument and solutions used: Mo and Ar are due to the
X-Ray source, Si is from the quartz sample carriers, Na is from the NaOH used to dissolve the HA, and Cl is from the HCl used to purify the HA (which is why it is only present in the purified sample). Of the four major impurities detected, Fe, Ca, and Ti are all typically found in soil, Co is not as common. Fe is the fourth most common element in the earth’s crust, with an abundance of 6.2%, Ca has an abundance of 4.66%, Ti has an abundance of 0.63%, and Co has an abundance of 0.0029%. Co’s natural abundance is low enough that the presence of it in the HA samples may not be due to a terrestrial source but rather as an impurity from a reagent.

![TXRF spectra of unpurified (black) and purified (green) Aldrich HA in NaOH.](image)

**Figure E.5.** TXRF spectra of unpurified (black) and purified (green) Aldrich HA in NaOH.

These results show that TXRF can be used to identify the metal impurities in HA, however, Aldrich HA does not have a certificate and there is no way to gauge its utility for quantifying the impurity concentrations. In order to quantify impurities, IHSS samples of Suwanee River HA and Elliott Soil HA
were prepared in $10^{-2} \text{ M NaOH}$ with the addition of Ga as an internal standard. With the addition of an internal standard, the software is able to approximate concentration based on the fluorescence peaks and their widths. Shown in Figure E.5 and Figure E.6 are the TXRF spectra of Suwannee River and Elliott Soil HA from IHSS. The blue labels are elements present due to the instrument setup and sample dissolution, and the red labels are highest concentration elements that are present due to impurities in the HA samples.

The IHSS HA samples are typically used as reference materials, but of the elements detected using TXRF, P and S are the only impurities detected that had a percentage listed on the IHSS datasheet. The measured and reported (when available) mass percentages are listed in Table E.2. Comparisons are limited due to the fact that the IHSS does not have a full characterization available, but S and P percentages are relatively close to the reported values for Elliott Soil. The ashing of the IHSS samples revealed homogeneity problems between samples from the same lot, so these samples probably had the same issue, which would account for the differences between measured and reported values.
Figure E.6. TXRF spectrum of IHSS Suwannee River HA dissolved in NaOH with an added Ga internal standard.

Figure E.7. TXRF spectrum of IHSS Elliott Soil HA dissolved in NaOH with an added Ga internal standard.
### Table E.2. Measured and reported mass percentages for IHSS Suwannee River and Elliott Soil HA.

<table>
<thead>
<tr>
<th></th>
<th>Suwannee River</th>
<th>Elliott Soil</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Measured (%)</td>
<td>Reported (%)</td>
</tr>
<tr>
<td>S</td>
<td>-</td>
<td>0.58</td>
</tr>
<tr>
<td>P</td>
<td>0.16</td>
<td>0.01</td>
</tr>
<tr>
<td>Al</td>
<td>2.4</td>
<td>-</td>
</tr>
<tr>
<td>K</td>
<td>0.51</td>
<td>-</td>
</tr>
<tr>
<td>Ca</td>
<td>0.12</td>
<td>-</td>
</tr>
<tr>
<td>Fe</td>
<td>0.19</td>
<td>-</td>
</tr>
<tr>
<td>Cu</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Br</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

**Efficacy of Centrifugation**

Solutions of colloidal silica in absence of HA were analyzed before and after centrifuging. A 1,000 ppm silica solution was found to contain less than 10 ppm silica after undergoing centrifugation. The 1 percent that was not removed via centrifugation was most likely due to the size distribution of the colloidal silica – that is, a small fraction of the silica has a diameter under 7 nm, even though the majority of the silica has a diameter of approximately 20 nm.

**Silica Dissolution**

When working with silica solutions, one of the issues is the potential for the silica to dissolve and form aqueous species instead of a colloidal dispersion. The dissolution studies were completed in order to insure the silica was present as a colloid and not an aqueous species. The results of the pH dependent dissolution study for a 1,000 ppm colloidal silica solution are shown in Figure E.8.
Figure E.8. Percent of Si dissolved in solution after centrifugation. Error bars shown are 2σ from replicates.

The majority of silica that remained in solution following centrifugation is due to the lower end of the size distribution of colloidal silica. As the pH is increased above 7, the percentage of silica not removed via centrifugation increases and is no longer only due to the size distribution of silica. In more basic conditions, silica begins to dissolve and form soluble aqueous species, two of the primary reactions are listed below (Equations E.2 and E.3).\(^{17,18}\)

\[
\text{SiO}_2 + 2\text{H}_2\text{O} \rightleftharpoons \text{Si(OH)}_4 \quad \text{E.2}
\]

\[
\text{Si(OH)}_4 + \text{OH}^- \rightleftharpoons \text{SiO(OH)}_3^- + \text{H}_2\text{O} \quad \text{E.3}
\]

Since the sorption studies were conducted at pH 6.5, the effects of the colloidal silica dissolving are negligible. These reactions prevent studies from being completed in more basic conditions, where HA
exhibits increased solubility. As OH⁻ concentrations increase, the silica dissolution becomes more of a factor.

**HA Sorption**

One of the issues with using colloidal silica for the quantification of HA is associated with size fluctuations. In order to determine the amount of HA that sorbed onto the silica, the silica is separated from the bulk mixture via centrifugation. The issue with this is that while HA ions exhibit sub-nanometer diameters, if any coagulation occurs within the solution due to the pH or supporting electrolyte, the coagulated HA molecules could be greater than the 7 nm lower limit for separation by ultracentrifugation.\textsuperscript{14,19,20} The common technique to decrease the risk of HA coagulation is to increase the pH of the system; this is not a viable option since doing so would cause more of the silica to dissolve. Approximately 10 percent of the HA present in the mixture was removed by centrifugation (represented by the line, the shaded area is 3σ error from the set of triplicates). Since a portion of the HA was removed by centrifugation, it became more difficult to determine the exact amount of HA sorbed onto the silica itself. As seen in the Figure E.9, 3 sets of silica concentrations had HA retentions that were within the error range of the HA lost to ultracentrifugation.
Figure E.9. Percent of HA sorbed onto colloidal silica (1,000 ppm HA contacting silica for 24 hours in 0.1 M NaClO₄). The line is the percent of HA lost via centrifugation, the shaded area is the 3σ error for the HA loss; error bars are 3σ calculated via triplicates.

Even with this issue, several conclusions can be drawn from the study. 1) Due to the similar percentages of HA sorbed at 0.1 ppm and 10,000 ppm HA concentration, the limiting factor to sorption is not the surface area of the colloidal silica. If surface area were limiting the sorption, the percentage of HA sorbed would increase as the silica concentration increases. This is one of the advantages of using colloidal silica: the surface area per gram is much higher due to its small moieties radius. 2) There is fairly minimal sorption of HA at a neutral pH. These results agree with other published works, in which maximum sorption occurred under more acidic conditions. This is primarily due to the fact that HA features pKₐ values of approximately 3 and 5 for its carboxylic acid groups. At pH 6.5, at which the studies were conducted, HA has a net negative charge due to both carboxylic acid groups being...
deprotonated. As such, it does not exhibit strong sorption properties with silica, which has a point of zero charge between pH 2 and 3.7,8 With both the HA and silica exhibiting negative charges, the sorption that does occur is not due to electrostatic interactions. One potential cause of the sorption that does occur is hydrogen bonding. On the surface of silica particles, there are Si(OH)_n molecules, which can interact with the COO⁻ groups of the deprotonated HA molecules.23

**Solvent Extraction in the Presence of Humic Acid**

When HA containing aqueous phases were contacted with TTA in xylenes, coagulation occurred, leading to the third phase formations shown in Figure E.10. The conditions of each sample are detailed in Table E.3. What appear to be bubbles at the interface between the two phases is actually a gel-like third phase that remained following centrifugation. This gel was present in all of the samples that contained HA. The presence of TTA in the organic phase seemed to shift the third phase’s presence from the interface to within the aqueous phase. This is evident when comparing sample 7 with 10 and 25 with 28 in Figure E.10. Samples 7 and 10 have identical aqueous phases; the only difference is 10 has TTA in the organic phase. The same is true for samples 25 and 28. With the addition of TTA, the opacity of the aqueous phases increased, pointing to an increase in undissolved particulate.

![Figure E.10](image-url)  
**Figure E.10.** Coagulation of HA following with xylenes and TTA.
The formation of these third phases prevents any further stability constant studies from being conducted. When a third phase occurs, an unknown quantity of the metal may exist within it. When this occurs, there is no way to ensure that the extractant system has reached equilibrium. Without confidence of equilibrium being reached, there is no way to accurately calculate the stability constants. As mentioned in Appendix C, further solvent extraction studies would be required under non-acidic conditions in order to be able to accurately measure the stability constants for HA via competitive solvent extraction.

Conclusions

Both TGA and TXRF are useful tools to provide more precise measurements for the characterization of HA samples. Ashing via TGA improves the precision of the measurements and decreases the likelihood of sample loss or contamination due to the controlled environment of the TGA. However, the

Table E.3. Conditions for each sample shown in Figure E.10.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Aqueous Phase</th>
<th>Organic Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10 ppm HA, 0.9 M NaClO₄, 0.01 M Acetate buffer, pH 4.09</td>
<td>Xylenes</td>
</tr>
<tr>
<td>4</td>
<td>10 ppm HA, 0.9 M NaClO₄, 0.01 M Acetate buffer, pH 4.09</td>
<td>0.075 M TTA in xylenes</td>
</tr>
<tr>
<td>7</td>
<td>50 ppm HA, 0.9 M NaClO₄, 0.01 M Acetate buffer, pH 4.07</td>
<td>Xylenes</td>
</tr>
<tr>
<td>10</td>
<td>50 ppm HA, 0.9 M NaClO₄, 0.01 M Acetate buffer, pH 4.07</td>
<td>0.075 M TTA in xylenes</td>
</tr>
<tr>
<td>22</td>
<td>10 ppm HA, 10⁻⁵ M Y, 0.9 M NaClO₄, 0.01 M Acetate buffer, pH 4.09</td>
<td>0.075 M TTA in xylenes</td>
</tr>
<tr>
<td>25</td>
<td>50 ppm HA, 10⁻⁵ M Y, 0.9 M NaClO₄, 0.01 M Acetate buffer, pH 4.09</td>
<td>Xylenes</td>
</tr>
<tr>
<td>28</td>
<td>50 ppm HA, 10⁻⁵ M Y, 0.9 M NaClO₄, 0.01 M Acetate buffer, pH 4.09</td>
<td>0.075 M TTA in xylenes</td>
</tr>
</tbody>
</table>
disadvantage of ashing still exists with the TGA in that the impurities are not characterized beyond confirming their existence. The TXRF appears to have potential for quantification of the impurities present in HA without requiring the digestion of the organic HA molecules. For further quantification beyond qualitative studies, a well-characterized HA sample should be analyzed with TXRF to determine if the sample matrix affects the concentrations determined via TXRF.

At neutral pH, there is minimal sorption of HA onto colloidal silica. This is likely due to both components having negative charges at pH 6.5. The minimal sorption that occurred is likely due to hydrogen bonding between the Si(OH)$_n$ species and the carboxylic acid groups on the HA molecules. While colloidal silica dispersions decreased measurement errors and increased consistency compared to sizing and weighing dry s, the size similarities between the colloidal silica and the HA decreased the precision of the sorption measurements. For future studies, a larger diameter colloidal silica dispersion (e.g. 100 nm colloids) would allow for the ease of use with colloidal silica while allowing for a better separation factor between the HA and silica in solution.

Both TTA and xylenes are factors in the formation of an HA coagulate. As such is it not an appropriate system to study the complexation of HA with Y. In order to compensate for this, future studies would require a different organic extractant and diluent. Coupled with the issues in extractant performance around pH 5 discussed in Appendix C, the best course of action for future work is potentially to perform the studies under basic conditions despite the formation of hydrolysis products.
References


APPENDIX F

THERMOGRAVIMETRIC ANALYSIS

Introduction
Thermogravimetric Analysis (TGA) utilizes a microbalance in a sealed furnace with a controllable atmosphere. This setup allows for very accurate and precise masses to be measured (mg – μg quantities) as a sample is being heated. The balance and the furnace combined into one sealed system allow for minimal measurement errors: 1) a properly loaded sample pan combined with a gradually increasing temperature allows for minimal sample loss; 2) the sealed atmosphere prevents the sample from interacting with airborne contaminants. As discussed in Appendix E, the traditional method for humic acid (HA) ashing uses a traditional annealing furnace and HA masses are measured before and after pyrolysis; there is a potential mass loss or increase during the multiple transfers, in particular due to water absorption by HA and ceramic crucibles. The use of a TGA for ashing samples increases the precision of the measurements without increasing the sample analysis time or amount of preparation required. Furthermore, the range of the TGA’s microbalance allows for minute sample sizes to be used.

Instrument Setup
The Pyris 1 TGA (Perkin Elmer, Waltham, MA) requires three gas lines: the Balance Purge, Sheath Gas, and N₂/Air. The Balance Purge should be an inert gas (N₂ or Ar) and is used to keep the balance chamber at a positive pressure so none of the gases coming off the sample affect the balance. The Sheath Gas is the gas that will be present in the furnace itself and can be inert or contain oxygen depending on the specifics of the sample being analyzed; the use of a sheath gas containing oxygen can promote more complete combustion of carbon containing materials. The N₂/Air gas is used to power mechanisms of the instrument (i.e. raising and lowering the furnace).
Two types of sample pans are commonly used: ceramic and platinum. The furnace and thermocouple are limited to 1000°C, so either pan can be used across the entire temperature range. The ceramic pans are more difficult to clean (due to porosity of the material), but are a fraction of the cost of platinum pans (<10%), so ceramic is typically used for this reason. The pan hangs on the quartz rod hanging down from the balance; the ceramic crucibles are one piece with an integrated hanger and the platinum pans rest in a carrier that hangs from the rod. The basic layout is depicted in Figure F.1.

**Calibration**

The Pyris software has three separate calibrations that must be performed to calibrate the instrument’s different measurements. The first calibration required is the Temperature Calibration, which calibrates the thermocouple’s reading with the actual temperature of the sample pan. Due to the design of the furnace, a second thermocouple cannot be used, so the temperature must be calibrated using the Curie Point of metal standards.

The Curie Point (or temperature) calibration relies on the magnetic transition that occurs in ferromagnetic materials at temperatures specific to the composition of the material. Below the Curie Point, the magnetic
moments of a ferromagnetic material are aligned with each other in an ordered manner; magnetic moments become disordered upon heating above the Curie Point (Figure F.2).1

![Diagram of ordered and disordered magnetic moments]

**Figure F.2.** The diagram on the left illustrates the ordered magnetic moment of the ferromagnetic material and on the right is the disordered magnetic moment when the ferromagnetic material is heated past the Curie Point and becomes paramagnetic.

The Thermocouple Calibration takes advantage of this phenomenon. The standards (Table F.1 lists the standards available from Perkin Elmer) are placed in the sample pan and a magnet is placed around the furnace below the sample pan (the magnet rests on the sheath gas inlet shown in Figure F.1). The presence of the magnet below the sample pan increases the measured mass of the ferromagnetic standards. The standards are heated to the Curie Point and become paramagnetic above the Curie Point; there is a perceived loss of mass due to the standards transitioning from being ferromagnetic (when the magnet pulls down on the sample) to paramagnetic (the magnet no longer is pulling the sample down. A plot of the change in mass for a single standard is shown in Figure F.3.

<table>
<thead>
<tr>
<th>Table F.1. Curie Point standards available from Perkin Elmer and their respective transitions temperatures.²</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Metal</strong></td>
</tr>
<tr>
<td>-----------</td>
</tr>
<tr>
<td>Alumel</td>
</tr>
<tr>
<td>Nickel</td>
</tr>
<tr>
<td>Perkalloy</td>
</tr>
<tr>
<td>Iron</td>
</tr>
<tr>
<td>HISAT-50</td>
</tr>
</tbody>
</table>
Figure F.3. The perceived mass loss due to an Alumel standard transitioning from ferromagnetic to paramagnetic.

The temperature at which the mass change occurs is the experimental Curie Point. This temperature will be used in conjunction with the accepted values to calibrate the thermocouple in the Pyris software. The following method describes the calibration steps for each calibration metal or for a mixture of calibration metals:

1) Ramp quickly (40°C per minute) up to approximately 50°C below the Curie Point.

2) Hold that temperature for 15 minutes to allow the temperature to stabilize.

3) Slowly ramp (4°C per minute) up to 50°C beyond the Curie Point of the calibration metal (the metal with the lowest Curie Point, if multiple metals are being used simultaneously).

4) The procedure is repeated for each subsequent higher calibration metal Curie Point.
The mass percentages are calculated for each point in terms of original total mass of the standards and the mass percent is plotted as a function of temperature. Curie Points are found from the derivative of this plot, which shows the peaks at each of the transitions (Figure F.4).

![Figure F.4](image)

**Figure F.4.** Mass percent and the derivative both in relation to temperature for a four metal Curie Point calibration with each transition labeled.

If the measured values are significantly (more than a few degrees) different than the literature values, we apply the most recent set of data and repeat the calibration operation. The balance is then calibrated between 1 and 20 mg. Finally, the furnace temperature is calibrated.
Trouble Shooting

If the temperature readout displays an unreasonably high temperature and the software freezes when anything is done to attempt to change the furnace temperature, the thermocouple has probably worn out from cycling between temperatures. To confirm this, unplug the black cable on the front of the TGA and measure the resistance between pins W and X. If the thermocouple is functioning properly, it should read 14 Ω. If not, an incomplete circuit is due to a thermocouple problem. The thermocouple can be easily replaced by the user, a new one is Perkin Elmer Catalog #03190253. To replace the thermocouple

1) Disconnect the gas tube on the side of the furnace.
2) Unclamp the black collar and remove it.
3) Lift the glass tube up over the furnace.
4) Remove the plate and the spring.
5) The black wire going down the ceramic rod is the thermocouple, unplug it from the base and gently pull it out of the furnace.
6) Using the old thermocouple as a guide, bend the new thermocouple so its length is about the same.
7) Feed the thermocouple into the furnace from below until it is 1-2 mm below the midpoint, centering it in the furnace. The height can be checked using one of the red caps that ships with the thermocouple. When the cap is placed into the furnace, the thermocouple should just barely touch.
8) Using tweezers, plug the thermocouple plug into the outlet next to the base of the ceramic rod.
9) Reassemble.

During normal use, the quartz rod that holds the sample pan can sometimes be knocked free. To remount the rod to the balance, rotate the top cover upwards and remove the balance cover, exposing the balance
assembly. Lower the quartz rod through the iris and loop the hook through the platinum wire. If the rod is not centered in the iris, loosen the two restraining bolts and carefully slide the balance assembly so that the quartz rod is centered in the iris. After centering the rod in the iris, close the iris using the adjustment lever so that there’s minimal space between the rod and the edges of the iris. Re-tighten the bolts and put the covers back into place. After adjusting the balance, always check the balance calibration with a weight.

**Figure F.5.** Balance assembly of the Pyris 1 TGA. (1) Quartz rod (2) Platinum wire (3) Balance restraining bolts (4) Iris adjustment lever.
References


APPENDIX G

COPY RELEASE INFORMATION

Figure G.1. Copyright release for Chapter 2 Batch Comparisons of Sr and Ba Retention and Capacities on Analig® SR-01 and Eichrom Sr Resins.