UNIVERSITY OF CALIFORNIA,
IRVINE

Electrospray Ionization Mass Spectroscopy analysis of solvent-solvent extraction complexes of lanthanide metals

THESIS

Submitted in partial satisfaction of the requirements
for the degree of

MASTER OF SCIENCE

in Chemical Engineering

by

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Thesis Committee:
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2016

DEDICATION

To

My mom and dad

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ACKNOWLEDGMENTS

My graduate school experience at University of California Irvine has a been both fulfilling and humbling. Trying to make my research valuable and useful and recognizing my own academic and intellectual ignorance was very humbling and an important part of the learning experience. However, making it through after struggling with methods that seemed like they would never work, has made it all the more worth it.

I would like to offer my sincerest thanks to those that have helped me along the way. Professor Nilsson's generous guidance, patience, and understanding has been no small part in me getting to where I am. He accepted me into his lab when I had a very weak chemical engineering background and no experience in nuclear chemistry, and I hope he feels I put that trust to good use. Professor Shaka and Professor Nguyen have both helped in ways they probably do not recognize—their questions during group meeting, directed at me and at others, have helped me approach problems in a more comprehensive manner, and importantly, understand the limitations of my research. For that I thank them.

For those in the lab, all of you have brought me in and were there when I needed help. Thank you. Alex, thank you for all the help in and out of lab.

Jessie, thank you for always believing in me. I'm so glad I got share this journey with you. Now with our baby, life will continue to present us with daunting challenges and joy, and we will meet it all together.

This work was partially supported by The Nuclear Regulatory Commission, Faculty Development Grant, Contract No: NRC-HQ-11-G-38-0037.

ABSTRACT OF THE THESIS

Electrospray Ionization Mass Spectroscopy analysis of solvent-solvent extraction complexes of lanthanide metals

By

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Master of Science in Chemical Engineering

University of California, Irvine, 2016

Professor Mikael Nilsson, Chair

To achieve industrial scale separation of long lived isotopes from spent nuclear fuel requires more work on the advanced chemistry involved. Analytical methods are important in gaining information that can support a more complete and thorough understanding of solvent extraction in spent nuclear fuel. Electrospray Ionization Mass Spectroscopy (ESI-MS) is a method used to determine masses of compounds in liquid samples. There is little understanding of how ESI-MS can be applied to analyzing compounds when extraction experiments are performed. In this work, extractions were done on Nd with di-(2-ethyl hexyl) phosphoric acid (HDEHP) and on Dy, La, Lu, Yb with varying amounts of tri-*n*-butyl phosphate (TBP) and/or dibutyl phosphate (HDBP). After extractions the organic phases were diluted 100 times in acetonitrile and the ESI-MS spectra were generated. There were five large peaks (and numerous less pronounced peaks) in the TBP/HDBP system that were distinguished by their isotopic spread and varied by the mass difference between the metals that were extracted. These five peaks were consistent for all metals tested. The results also showed that there is replicability in the experiments, and that species existing in solution may possibly be determined by their masses in ESI-MS spectra.

Though comprehensive species identification has not been achieved at this point, this evidence shows ESI-MS may be a useful tool in determining some of the more common liquid phase extraction complexes.

INTRODUCTION

The energy demand of a growing world population continues to be a daunting challenge. Nuclear power has the capacity to produce and meet baseload electricity demands, and produces the least amount of carbon dioxide among the varying methods of electricity generation (except for wind)[1]. Nuclear power is the safest method for electricity generation by the kilowatt hour of electricity produced, but still has the requirement to deal with the radioactive waste produced. This waste has the potential to cause environmental disaster, and considering the length of time that some of the waste can remain active, an accident can happen many years later. With proper management, nuclear waste can be contained and controlled resulting in a diminished chance of environmental catastrophe.

The longevity of the radioactivity in spent nuclear fuel is due to long lived radioactive isotopes of some lanthanides, actinides, and some other elements which, if extracted, would result in separation of both the short lived and long lived isotopes allowing for smaller volumes of long lived radioactive waste. This could make transportation and storage of the waste components easier. Safety concerns about radioactive nuclear waste are not the only driving force for the separation and recycling of spent nuclear fuel.

Economic viability of obtaining uranium is an important factor to consider when thinking about the cost of electricity produced by nuclear reactors. Since there is a finite amount of uranium on Earth, the amount of easily obtainable uranium would decrease over time, creating another incentive to begin recycling nuclear waste.[2] There are numerous factors that could increase the lifetime of the uranium mined, one of which is nuclear fuel reprocessing. Recycling nuclear waste would increase the length of use of already mined uranium and would further decrease carbon emissions by lowering the demand for new ore to be mined. The complex and

advanced chemistry involved in nuclear fuel reprocessing means that there is much to be figured out before scaling up processes efficiently and safely. A main method of fuel recycling is solvent extraction in which the analyte of interest is separated by an organic phase contacted with an aqueous phase. This usually involves an extraction reagent which binds with the analyte in the aqueous phase and extracts the analyte into the organic phase.

In the context of nuclear fuel extraction processes, the analyte of interest is an aqueous phase metal ion, often a lanthanide or an actinide, which binds to an extractant and is transferred to the organic phase. Knowing the complexes that the extractants form with the metal ions can provide insight into the extraction mechanisms. Analyzing the mass of a compound with a mass analyzer can be difficult for organometallic compounds because of the volatility required to bring the compounds into the gas phase. Electrospray Ionization Mass Spectroscopy (ESI-MS) is an analytical tool used to determine masses of compounds in a liquid sample which may help in determining the complexes formed by the extractants and metals ions. Electrospray Ionization Mass Spectroscopy can generate data quickly: each sample run takes anywhere from seconds to minutes, each run only requires 10-100 μL and the accuracy of the method can allow rapid determination of species in the sample. These points combine to provide strong time and financial incentives in investigating the utility of ESI-MS in the chemical systems of lanthanide extraction. However, the masses detected by ESI-MS may be a figment of the ionization process. Determining if the observed masses correspond to complexes in the liquid phase (and are not only created by the ionization process) is an important step in finding out if ESI-MS can be a useful method of analysis.

This work will consist of two parts: first, the replication of previous work on the extraction of Nd by di-(2-ethylhexyl) phosphoric acid (HDEHP), and second, ESI-MS analysis of the

extraction of Dy, La, Lu, Yb with varying amounts of tri-*n*-butyl phosphate (TBP) and/or dibutyl phosphate (HDBP).

SPECIFIC GOALS

The dilution of the organic phase in preparation for running the sample through the Electrospray Ionization Mass Spectrometer (ESI-MS) creates a different chemical environment than is naturally occurring during the extraction. Therefore, determining the method of dilution that can produce consistent and reproducible results is an important preliminary goal. Once this goal is reached, the work could proceed with a stronger focus on the ionization process as a source of error.

Due to the dilution step and ionization process required for ESI-MS, it is currently unknown how the observed ions on a mass spectrum correspond to complexes that exist in the organic phase after a solvent-solvent extraction. The specific goal of this work is to determine if the spectra generated by ESI-MS can be useful in determining complexed species, considering the dilution step and the ionization process.

BACKGROUND

A. Preface

The background section is not a comprehensive overview of the topics discussed. The purpose here is to explain the different concepts to the extent that a common link can be drawn between different aspects of the work.

B. Solvent Extraction

Solvent extraction is a method used to change the concentration of a solute in two immiscible fluids. These immiscible fluids are typically an organic phase liquid and an aqueous phase which is usually water.[4] The solute is transferred from one of these phases to the other, which results in a change in concentration of the solute in the respective phases. This transfer of solute happens once the phases come into contact and if enough time passes, an equilibrium is reached between the two phases. The equilibrium is represented by the distribution ratio (see Eq. 1) which is the ratio of the concentration of the solute in the organic phase divided by the concentration of the solute in the aqueous phase.

$$\boldsymbol{D = [A]_{org}/[A]_{aq}} \quad \textbf{(1)}$$

A benefit of solvent extraction is that in a complex mixture consisting of many solute species a specific solute can be selectively removed. Since the organic and aqueous phases are immiscible, the selected solute can be physically removed from the two phase system by removing the extracting phase. An example is that of the Plutonium Uranium Redox Extraction (PUREX) process, in which an acidic aqueous phase contains dissolved metals (typically from spent nuclear fuel or irradiated materials)[4] and an organic phase consisting of tri-*n*-butyl

phosphate (TBP). The extractant, TBP, selectively extracts Uranium (U) and Plutonium (Pu) by a solvation mechanism[5] into the organic phase (shown as Equation 2) which can be separated and the result is a solution containing only the solutes of interest.

$$M_{aq}^{n+} + n(NO_3^-)_{aq} + mTBP_{org} \rightleftarrows [M(NO_3)_n(TBP)_m]_{org} + water \quad \textbf{(2)}$$

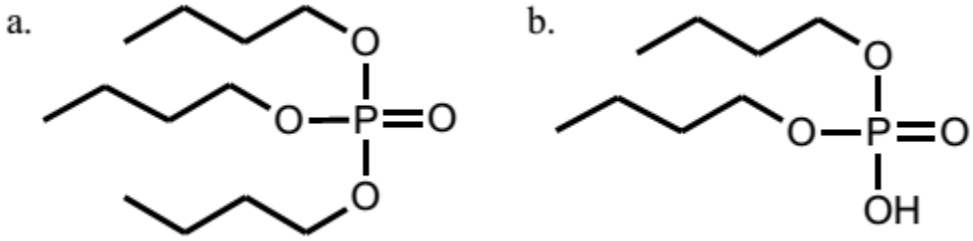

Figure 1. Structures of TBP (a) and HDBP (b).

The specificity of solute extraction is a motivation for understanding the interactions between solvent, solute and extractant. In the example of the extraction of U and Pu by TBP, the system will be emitting radiation due to the sample being irradiated, or coming from dissolved nuclear fuel. The radiation causes TBP to fragment in a variety of ways, but one of the important radiolysis products is dibutyl phosphoric acid (HDBP).[6] HDBP is an acidic chelating extraction reagent, which means that its extraction strength is influenced by the acidity of the solution. This has led to problems in the PUREX process in which radiolytic degradation of TBP, creating HDBP, leads to a dynamic extraction system which makes modeling difficult. This phenomenon of TBP fragmentation to HDBP and their different mechanisms of extraction is motivation for this work to focus on the TBP/HDBP system.

C. Electrospray Ionization Mass Spectroscopy

Electrospray Ionization Mass Spectroscopy is an analytical method used to determine masses of chemical species in solution. Compared to other means of volatilizing a compound for mass analysis, such as electron ionization, field desorption, and fast atom bombardment, ESI-MS results in moderate fragmentation of the compound, likely making it the best option currently available for organometallic compound mass spectroscopy.[10] There are a number of different types of ESI-MS machines, and the one used in this work was a time-of-flight (TOF) analyzer, which will be the focus of this section.

How ESI-MS works (see Figure 1):

1. High voltage applied in spray needle
    a. 2-5 kV are applied to the spray needle to cause charges to accumulate in the injected sample via the electrophoretic mechanism
2. Taylor cone
    a. The deformation in the liquid caused by surface tension
3. Aerosolizing of the sample
    a. If the electric field is strong enough a fine jet of aerosolized sample is emitted from the Taylor cone
4. Heated gas (nitrogen, or carbon dioxide are common) causes nebulization to decrease solvent in the droplets
5. Desolvation of the droplets (sample is usually diluted with water, methanol, acetonitrile, or a mix of any of them)

6. Rayleigh limit
    a. This is the limit at which surface tension in a droplet is equivalent to the electrostatic repulsion within the droplet
7. Coulombic fission
    a. This occurs when the Rayleigh limit is reached, and causes the droplet to release fine sprays of fluid
8. Process is repeated until there are gas phase ions
9. Gas phase ions reach the mass analyzer resulting in a spectrum of abundance of fragment with respect to their mass to charge ratio (m/z)

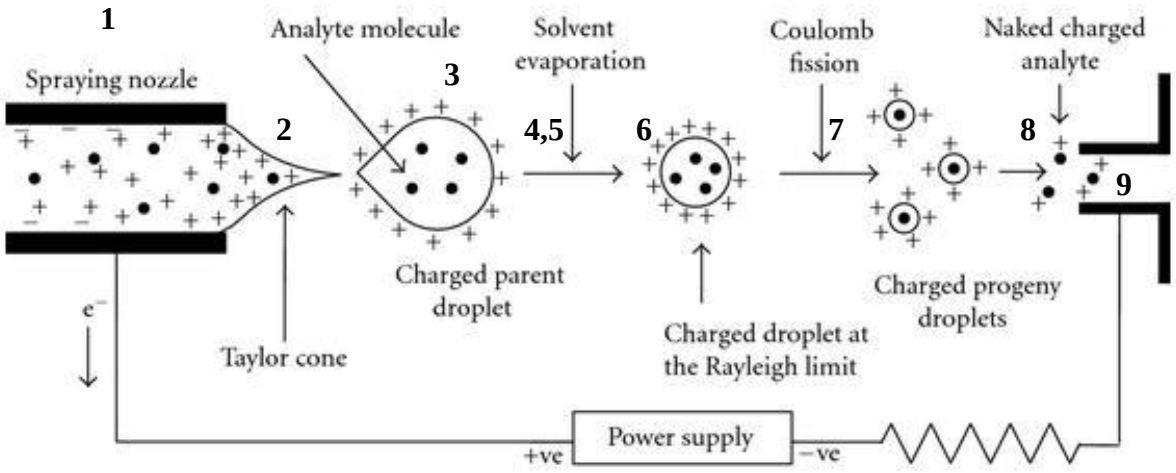

Figure 2. A schematic for the processes involved in a general ESI-MS machine. Numbers correlate to steps above under "How ESI-MS works".

For a TOF ESI-MS machine, the kinetic energy of the molecule is:

$$E_k\ (m, v) = \frac{1}{2} m v^2 \qquad \textbf{(3)}$$

In equation **(3)** $\boldsymbol{v}$ is the velocity vector, but since TOF mass spectrometers are usually of linear design this can be simplified into:

$$E_k\,(m, v_x) = \frac{1}{2} m {v_x}^2 \qquad \textbf{(4)}$$

An important note is that the particles are accelerated before entering a free flight zone, and this acceleration is due to an electric potential acting on the charged particles. Because of this, the particles enter the free flight zone with equivalent kinetic energies so equation **(4)** can be rearranged to:

$$v_x = \sqrt{\frac{2E_k}{m}} \qquad \textbf{(5)}$$

Since velocity is also defined as:

$$v_x = {}^{x}/_{t} \qquad \textbf{(6)}$$

Then the time the particle spends in the TOF mass spectrometer can be given as a function of particle mass by combining and rearranging equations **(5)** and **(6)**:

$$t = \frac{x}{\sqrt{\frac{2E_k}{m}}} \qquad \textbf{(7)}$$

Kinetic energy can also be represented by the charge (z) of the particle times the electric potential (U):

$$E_k = E_p = zU \quad \textbf{(8)}$$

(this occurs in the region of acceleration) which can give the result of time being proportional to the square root of mass to charge ratio:

$$t = \frac{x}{\sqrt{\frac{2zU}{m}}} = \frac{x}{\sqrt{2U}}\sqrt{\frac{m}{z}} = k\sqrt{\frac{m}{z}} \quad \textbf{(9)}$$

Once the particle is accelerated by the electric potential within the ESI-MS and travels with its mass dependent velocity through the free flight zone, a detector at the end can calculate the mass to charge ratio as a function of time. Once the data is collected a spectrum is generated as exemplified in Figure 3.

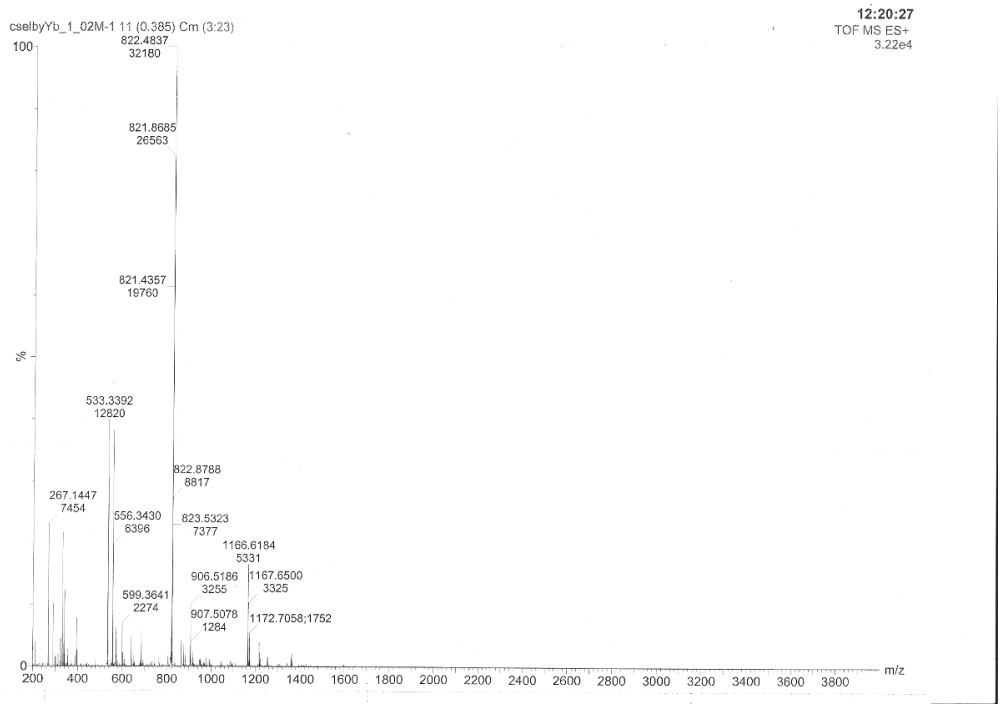

Figure 3. An example ESI-MS spectrum: aqueous phase of 0.2 M HNO_3 with 0.001 M Yb contacted with 1M TBP in n-dodecane. Organic phase was diluted 100 times in acetonitrile before ESI-MS run.

The ESI-MS spectrum gives the counts per second of each mass encountered, as shown in Figure 3 in the top right corner with the peak at 822.48 having an intensity of 3.22e4 (3.22e4 = $3.22x10^4$) counts per second. The spectrum can also show a particular fragmentation of a parent molecule, although the complexity of the sample can make this more difficult because the process of getting the sample into the gas phase can cause changes in the solution and as a result, change the molecules present.[7] However, the mass difference between peaks may be able to support an explanation for a particular molecules fragmentation. This can be used as supporting evidence of a particular parent molecule if the parent molecule is unknown.

Another important piece of information is that the ESI-MS spectrum can show variations in a molecule's mass based on the isotopic abundance of the molecule's constituent atoms. For example, a molecule that contains Dy, which has seven commonly occurring isotopes, will have

an isotopic spread that appears different on an ESI-MS spectrum from the same molecule with Dy replaced by La, which has one commonly occurring isotope (99.91% natural abundance of La-139).

D. Previous Works

The use of ESI-MS on solvent extraction systems is relatively new, and the amount of published results in scarce. This section will cover some of work already done, both as a background for methods and results for ESI-MS in this field, but also to offer a comparison of those methods and results to those of this work.

a. Antonio M. et al. (*Separation Science and Technology*, 2008; vol. 43)

Antonio et al. performed extractions of 1 M Nd in 0.1 M HNO_3 with either 0.1 M HDEHP or di-*n*-hexyl phosphoric acid (HDHP) in dodecane. The generated spectra showed evidence of a parent molecule consisting of three monodeprotonated dimers of the extractant. The strongest peak was with the loss of one of these monodeprotonated dimers (two HDEHP molecules) from the parent ion, showing evidence that in the gas phase two HDEHP extractant molecules may be more weakly bound to the metal than the other four HDEHP molecules.

They performed ESI-MS measurements with varying cone voltage as a secondary experiment and found that the species observed on spectra were the same but their relative abundances changed as a function of cone voltage.

The most significant finding was evidence for the preservation of liquid phase metal-ligand complexes into the gas phase.[11]

b. Scharf C. et al. (*Metallurgical and Materials Transactions B*, 2005; vol. 36B)

Scharf et al. performed extractions of Nd with an organic phase of 20% volume HDEHP and 80% volume kerosene. The aqueous phase consisted of 20 g/L of Nd.[13] The generated spectra and species identified were almost identical to that of Antonio et al.

c. Groenewold G., Gaumet J. (*Journal of Mass Spectrometry*, 2011; vol. 46)

Groenewold and Gaumet performed extractions of Ce^{3+} with TBP. The concentrations were 0.28 or 0.3 mM for Ce and 1.8 to 0.003 mM for TBP. It was noted that previous works on the Ce containing solutions showed that the Ce was present in a significant amount as the +2 charged complex. The ESI-MS results, however, showed a predominance of +1 charged species indicating that the species present in solution were likely changed in the ionization process.

d. Leclerc E., Guillaumont D., Guilbaud P., Berthon L. (*Radiochem. Acta*, 2008; vol. 96)

In this work HDEHP and HDHP were used as the extractants on Nd and Eu. HDEHP and HDHP concentrations were 0.15 M in dodecane while the metals were 0.01 M in glycolic acid with pH=3. The contacting step consisted of 1 mL of organic phase to 4 mL of the aqueous phase. The results were very similar to those found in Antonio et al. and Scharf et al.

EXPERIMENTS AND METHODS

Di-(2-ethylhexyl) phosphoric acid (HDEHP) was used in the extraction of Neodymium (Nd) to replicate the data from Antonio et. al. This extraction was carried out as multiple experiments with varying aqueous phases: 0.1 M Nd, 0.2 M Nd and 1.0 M Nd, all in 0.1 M HNO_3. For all experiments the HDEHP was at 0.1 M in n-dodecane. The organic and aqueous phases were vortexed together in equal volumes for 15 minutes and centrifuged for 5 minutes. The resulting organic phase was separated allowing for multiple ESI tests. Several methods of dilution were used in preparation of the organic phase for ESI analysis:

1. 10 times in ethanol then 1,000 times in 50/50 acetonitrile and water mix
2. 10,000 times in 50/50 acetonitrile and water mix
3. 1,000 times in 50/50 acetonitrile and water mix
4. 100 times in 50/50 acetonitrile and water mix
5. 1,000 times in acetonitrile
6. 100 times in acetonitrile
7. 1,000 times in water
8. 10 times in ethanol and 100 times in 50/50 acetonitrile and water mix
9. 1,000 times in 50/50 ethanol and isopropanol mix

ESI control spectra of acetonitrile, water, ethanol, and 0.1 M HDEHP in n-dodecane contacted with non-metal loaded 0.1 M HNO_3 were made. Glassware bought specifically for use in ESI-MS experiments was used and not washed in the lab sink, but rinsed with acetonitrile between experiments. All of the contacted samples were made in clean disposable glass vials, and cryotubes were used in the dilution of the organic phases into acetonitrile.

Tri-n-butyl phosphate (TBP) and di-n-butyl phosphoric acid (HDBP) were the next extraction reagents analyzed. The organic phases consisted of TBP and HDBP in n-dodecane with the following concentrations:

1. 1 M TBP: 0 M HDBP
2. 0.75 M TBP: 0.25 M HDBP
3. 0.5 M TBP: 0.5 M HDBP
4. 0.25 M TBP: 0.75 M HDBP
5. 0 M TBP: 1 M HDBP

The aqueous phase was either 2 M or 0.2 M HNO_3, both containing a lanthanide at 10^{-3} M. Organic phases 1-5 were contacted with 2 M HNO_3 and another set of organic phases 1-5 were contacted with 0.2 M HNO_3. ESI spectra were first taken of organic phases 1-5 before contact with the aqueous phase as a control. Spectra were then taken of organic phases 1-5 contacted with a non-metal loaded aqueous phase as a secondary control. Lastly spectra were taken with organic phases contacted with metal loaded aqueous phases with one of the following: La, Dy, Yb, and Lu all at 10^{-3} M. After vortexing for 15 minutes with the aqueous phase and 5 minutes of centrifugation all of the organic phases were pulled off. These organic phases were diluted 100 times in acetonitrile in preparation for ESI-MS.

The same glassware used in the HDEHP extraction experiments was used in the TBP/HDBP extraction experiments. The same brand of disposable glass vials and cryotubes (Qorpak and Fisher Scientific respectively) were also used for the TBP/HDBP extraction experiments.

The ESI-MS machine was an LCT Premier by Micromass Technologies. The ESI-MS skimmer voltage was kept constant at 30V for all runs to prevent excess fragmentation or loss of sensitivity.[12] Methanol was the carrier solvent for all ESI-MS runs.

RESULTS AND DISCUSSION

A. HDEHP Extraction System—Replication of Antonio et al.

The experiments conducted to replicate the work by Antonio et. al., which was the extraction of 1 M Nd by 0.1 M HDEHP (structure shown in Figure 4), initially showed no similarities.

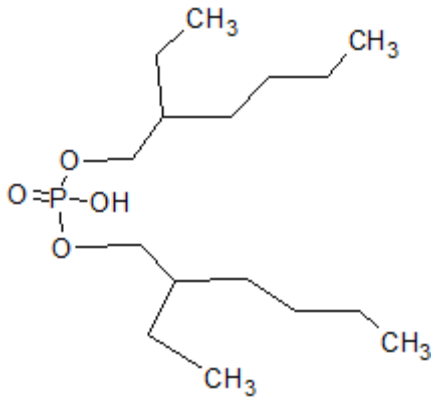

Figure 4. Structure of the extractant HDEHP.

The complexation peaks that were present in both Antonio and Scharf papers were not observed. Further, there was no evidence of ionized monomers, dimers, trimers or other higher aggregates of HDEHP. The experiment was redone for 0.1 M Nd, and then for 0.1 M Er and 0.1 M Dy. This was to see if there were any Nd extraction peaks that were not listed as a part of the Antonio and Scharf papers. If the peaks were consistent for the Er and Dy extractions, (varying by the mass difference between Nd and Er or Dy) then there would be evidence for complexes not observed previously. This was not the case as all the largest peaks were the exact same for all three metal ions as well as for both concentrations of Nd.

A process of elimination was undertaken to determine why the experimental results were not matching that of Antonio. As shown by Gannaz[15] the dilution of the organic phase is a critical step in getting observable complexes by ESI-MS. This means both the dilution amount and the

chosen diluents are of critical importance. The dilution protocols listed in the experiments and methods section were all used for the 1 M Nd extraction. Peak intensities changed depending on the amount of dilution, and the water only dilution did not work because water could not solvate the organic phase. The only dilution method that yielded peaks corresponding to monomers, dimers, trimers and higher aggregates of HDEHP was a 100 times dilution of the organic phase in acetonitrile. However, one consistency among all dilution methods was a large peak at 739.6 m/z (and lower intensity peaks at 381.2, 1017.6, and 390). The next step was to take spectra of HDEHP blanks, as well as an ethanol, acetonitrile, and water solvent blanks.

All of the solvents contained the 739.6 peak which meant that there was contamination of either all of the solvents or of the glassware used.

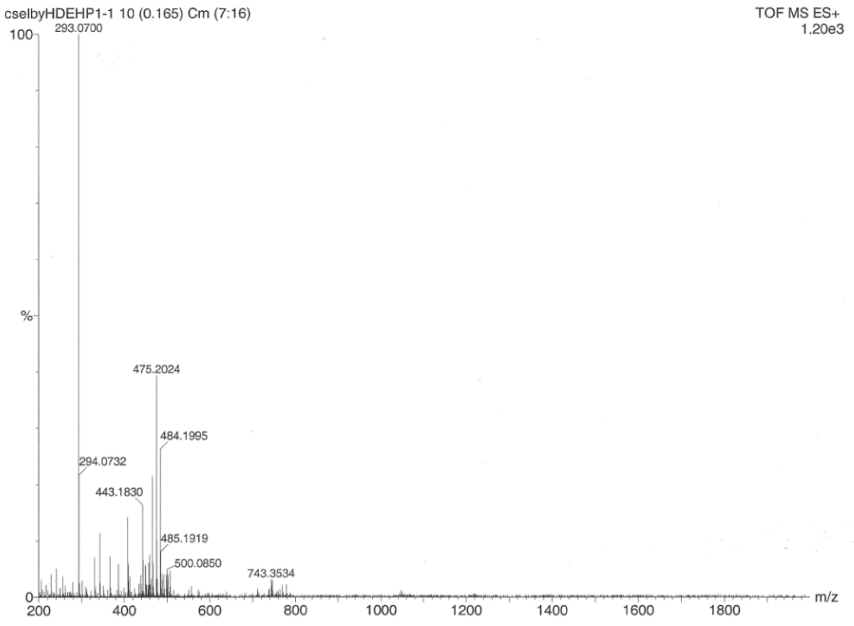

Figure 5. ESI spectrum for 0.1 M HDEHP in n-dodecane after contact with 0.1 M HNO_3 (no metal).

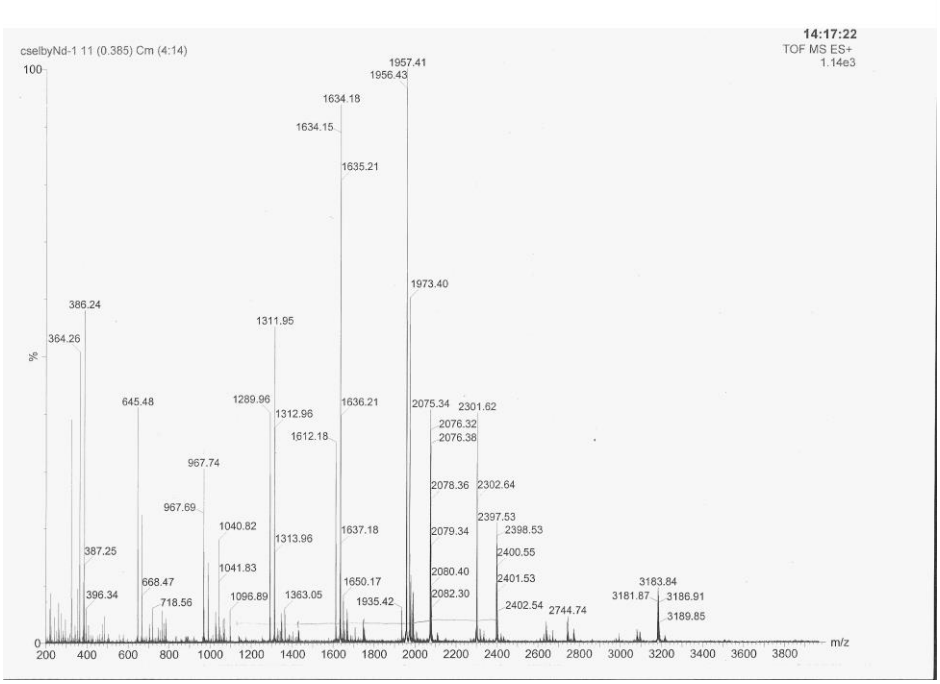

Figure 6. ESI spectrum for 0.1 M HDEHP in n-dodecane contacted with 0.1 M Nd in 0.1M HNO_3, diluted 100 times in acetonitrile.

New glassware was purchased, as well as new acetonitrile, water and ethanol (from Pierce via Thermo Fisher for acetonitrile and water, ethanol was from Alfa Aesar). Blank spectra were run for the new solvents and all of them were void of the 739.6 peak. The HDEHP blank sample (Figure 5) resulted in very low overall signal compared to other blanks, which were at least an order of magnitude greater.

The extraction of 0.1 M Nd was carried out again, and diluted 100 times in the new acetonitrile. The spectrum is shown in Figure 6, where the peaks identified as complex masses are 1108.8, 1269.9, 1431.0, 1753.1, 2075.1. All of the complexes observed by Antonio et al. were present in the spectrum. The experiment was redone for both La and Lu. Both extraction ESI spectra showed no Nd equivalent complexes which were calculated by using the mass difference between Nd and La or Lu.

However, the spectra did not contain the same relative peak intensities as Antonio et al., which can be due to the differences in the ESI-MS settings for the ionization process, the dilution, and the carrying solvent. They did a 10 times dilution in ethanol first and then a 1000 times dilution in a 50/50 mix of water and acetonitrile, compared to the 100 times dilution in acetonitrile in this work. Both methanol and acetonitrile were tried as the carrier solvent and there was no observed difference in the resulting spectra. The aggregation peaks, which had higher intensities than the complexation peaks, were not subtracted from the spectra. This work shows that there is replicability in the ESI-MS analysis of this extraction system, even taking ESI-MS operational differences into account. With a different dilution method, the observed spectra were different but similar, and all of the complexes previously observed were present.

B. TBP and HDBP Extraction Systems

The near replication of the data by Antonio et al. and Scharf et al., lends support to the application of the technique to other extraction systems. Therefore, the TBP and HDBP extraction system was tested with organic phase samples in n-dodecane at the following concentrations:

1. 1 M TBP: 0 M HDBP
2. 0.75 M TBP: 0.25 M HDBP
3. 0.5 M TBP: 0.5 M HDBP
4. 0.25 M TBP: 0.75 M HDBP
5. 0 M TBP: 1 M HDBP

These samples were contacted with non-metal loaded 2 M or 0.2 M HNO_3 aqueous phases. These were the blank spectra for this extraction system. This allows elimination of peaks present in the non-metal loaded sample from the ESI-MS spectra of the metal contacted organic phases

(see Appendix 16-22). Also, the concentrations for all four metals (Dy, La, Lu, and Yb) in the TBP/HDBP extraction experiments were 0.001 M.

The first extraction was of Dy and after subtraction of the blank peaks there were many possible complex peaks. These possible complex peaks are listed in table 1.

Table 1. Dy extraction by the organic phases 1-5. Dy concentration was 0.001 M and either in 2 M or 0.2 M HNO_3, as listed at the top of the table. The value for the Complex peak column is the highest m/z peak in an array of isotopes for a particular complex. Peak intensity was given on the spectra, where a value of 0 means the peak was not observed.

	1-2M	2-2M	3-2M	4-2M	5-2M	1-0.2M	2-0.2M	3-0.2M	4-0.2M	5-0.2M
Complex Peak	peak intensity	peak intensity	peak intensity	peak intensity	peak intensity	peak intensity	peak intensity	peak intensity	peak intensity	peak intensity
1352	583	0	0	0	0	137	0	0	0	0
1422	0	525	665	776	699	0	0	301	433	683
1654.7	0	0	0	118	94	0	0	76	73	0
1866.8	0	0	1370	1050	622	0	247	646	572	535
1895.8	0	0	650	504	310	0	135	239	280	260
1922.8	0	0	137	0	0	0	35	65	0	25
2130	0	0	0	89	64	0	48	50	0	0
2311	0	353	576	731	307	0	283	533	320	188
2340	0	540	720	690	185	0	250	280	165	100
2369	0	0	250	256	75	0	110	75	50	38
2445.9	0	0	30	30	27	0	0	20	25	28
2472	0	182	156	200	54	0	0	50	45	28
2519	0	0	27	36	27	0	20	22	22	17
2535	0	0	0	0	67	0	28	55	37	36
2550	0	0	157	170	60	0	63	65	50	30
2564	0	0	0	0	40	0	20	20	28	24
2578	0	0	110	110	27	0	40	22	25	18
2618	0	0	45	40	0	0	20	20	15	0
2685	0	0	40	66	68	0	20	60	65	60
2892	0	0	20	47	30	0	17	43	35	0
3004	0	0	20	0	27	0	0	0	30	27
3447	0	0	0	0	42	0	0	0	0	0
3476	0	0	0	0	19	0	0	0	0	0

As shown in table 1, only one complex observed was formed by TBP alone at mass of 1352. Almost all of the other complexes formed were observed in organic phase 5 which only contained HDBP. This result is evidence for complexes mostly containing HDBP, especially the more common complexes. Furthermore, since HDBP is an acidic extraction reagent, it should extract more strongly in the 0.2 M HNO_3 aqueous phase. The results show higher intensities for the 2 M aqueous phase contacting, which means that the acidity of the aqueous phase may have an influence on the ionization process.

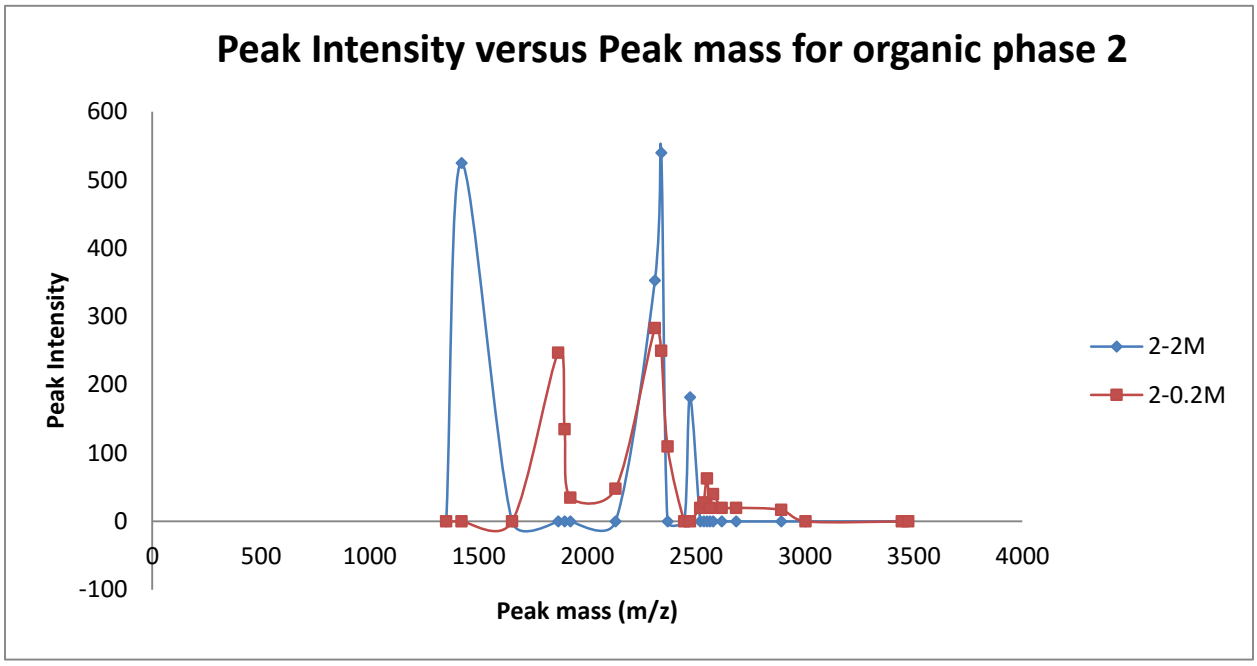

Figure 7. Peak intensity plotted against peak mass for all observed possible peaks in the extraction of 0.001 M Dy by organic phase 2. Data taken from table 1 and plotted for both 2 M and 0.2 M HNO_3 aqueous phases.

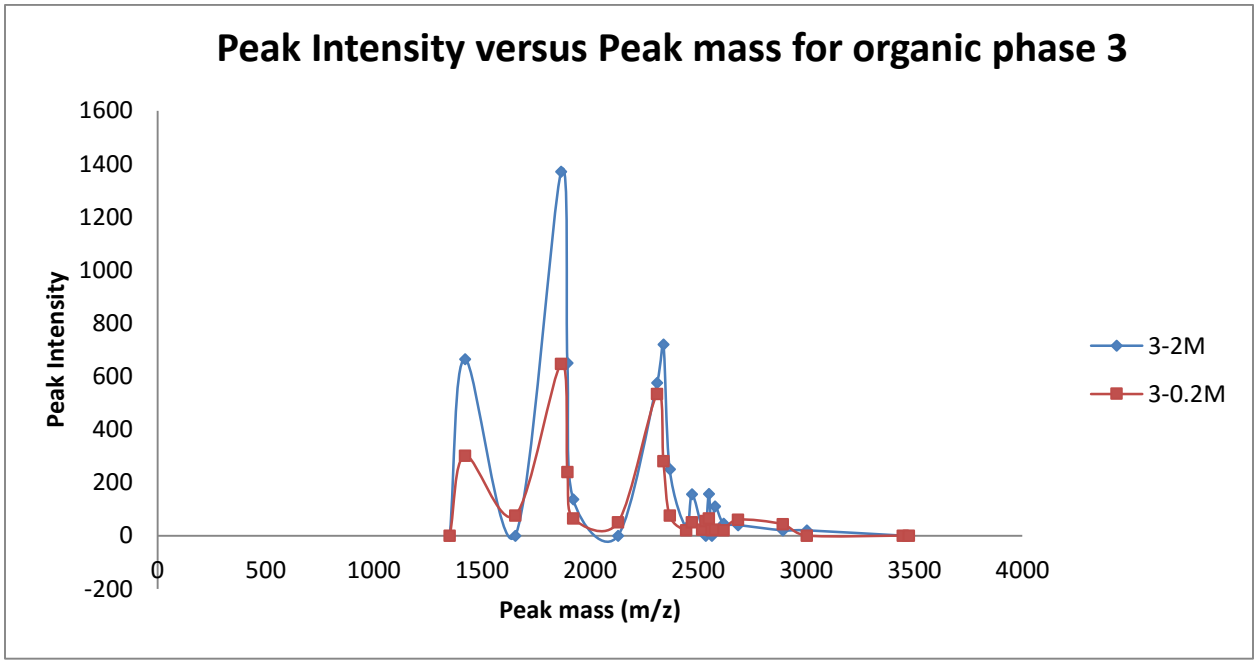

Figure 8. Peak intensity plotted against peak mass for all possible peaks in the extraction of 0.001 M Dy by organic phase 3. Data taken from table 1 and plotted for both 2 M and 0.2 M HNO_3 aqueous phases.

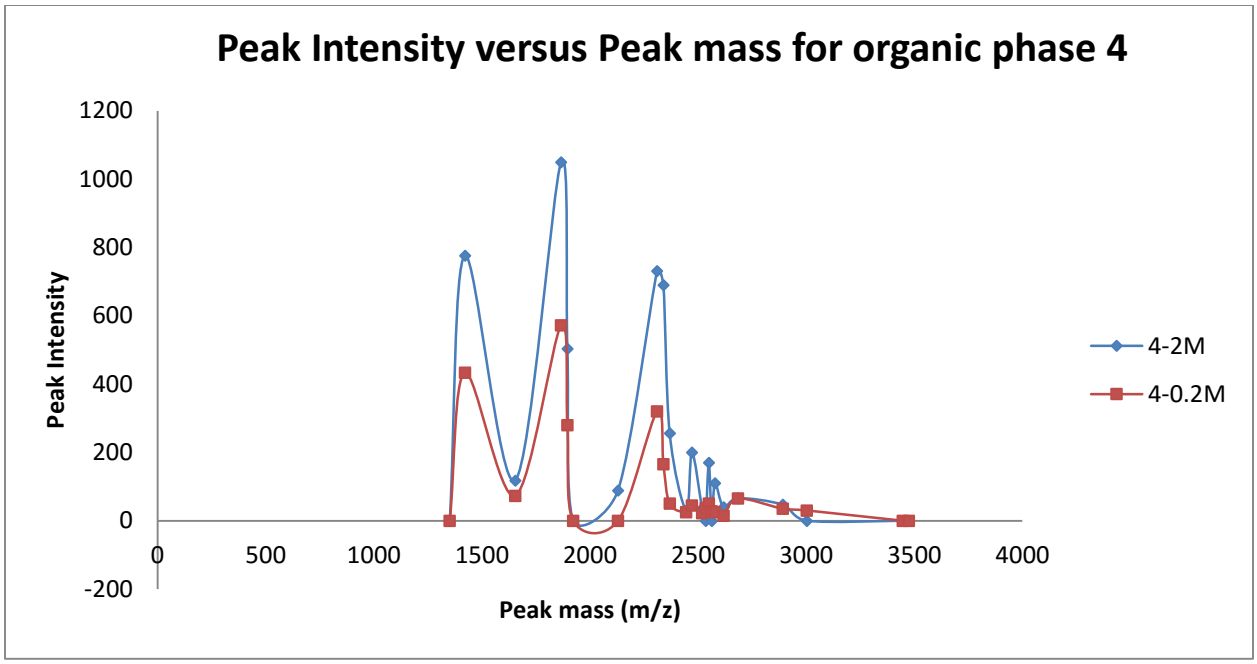

Figure 9. Peak intensity plotted against peak mass for all possible peaks in the extraction of 0.001 M Dy by organic phase 4. Data taken from table 1 and plotted for both 2 M and 0.2 M HNO_3 aqueous phases.

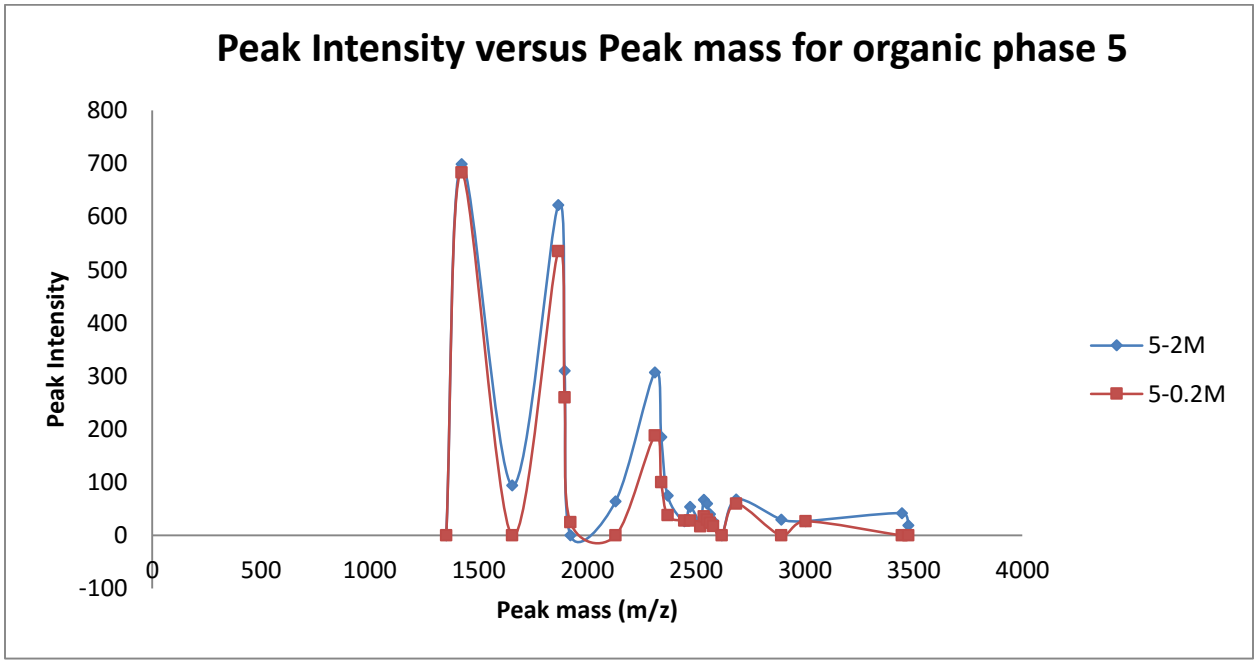

Figure 10. Peak intensity plotted against peak mass for all possible peaks in the extraction of 0.001 M Dy by organic phase 5. Data taken from table 1 and plotted for both 2 M and 0.2 M HNO_3 aqueous phases.

As shown in Figures 7-9, the intensity of the complex peaks is lower in the 0.2 M HNO_3 aqueous phase than the 2 M HNO_3. However, in Figure 10, the intensities are much closer in value. The organic phase in Figure 10 consisted of only HDBP, which means that TBP itself may play a role in lowering the ESI-MS signal in organic phases 2, 3 and 4 when contacted with the 0.2 M HNO_3 aqueous phase. This finding is neither comprehensive, nor conclusive, but is a piece of data to be considered. That the extraction molecules themselves may cause structural changes in the complexes, or a change in their natural abundance in solution due to the ionization process. ESI-MS is not typically used as a quantitative method, and it is important to note that peak intensity in these spectra does not warrant quantitative findings. Here, it was important to gain data on how the spectra varied due to their differences in both the aqueous and organic phases.

Many of the possible complex peaks observed for the extraction for Dy were also seen in the extraction of La, Lu, and Yb. The possible complex peaks in the La, Lu and Yb spectra were the same as the Dy peaks, but the peak masses varied by the difference in mass with Dy. The most intense peaks in the Dy extraction (as seen in Table 1) were 1352, 1422, 1866.8, 1895.8, 2311, and 2340. All of these peaks showed strong signal as well for La, Lu and Yb extractions and will be the basis of the spectra shown in Figures 11 through 16. The larger possible complex masses also contain the possibility of being either dinuclear or trinuclear complexes (see Appendix 3). The largest observed possible Dy complex peaks, 3447 and 3476 were not observed in the corresponding La extraction, but were observed in the Lu and Yb extractions as possible trinuclear complexes.

The method used to determine which peaks to investigate can be observed most clearly in Figures 11, 12, 13 and 15. Figures 11 and 12 are spectra for the same complex, but for the

extraction of Yb and Dy respectively. The mass of this complex is 3 monodeprotonated dimers plus the corresponding metal:

$$3HDBP + 3DBP^{-} + Dy^{3+} + H^{+} = 1422 \quad \textbf{(10)}$$

The isotopic spread is the predominant factor in determining which peaks are possible metal containing complexes. It is for this reason that Dy, which has 7 stable isotopes, was chosen as a basis to compare the other extractions. Once the initial spectra of Dy were made, they were scanned for peaks that had at least 7 isotopes and marked down, then compared to the spectra for the extractions of the other metals. This is the method used to generate the data in Appendix 3.

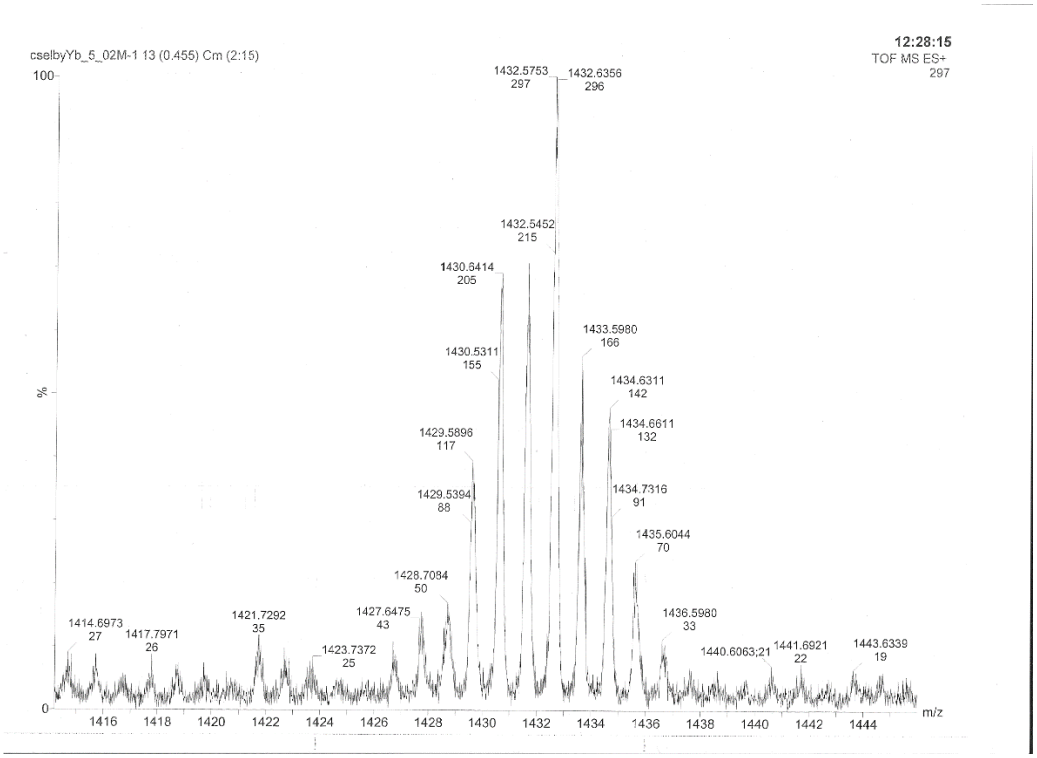

Figure 11. The ESI spectrum for organic phase 5 contacted with 0.001 M Yb in 0.2 M HNO_3 zoomed in on complex 1432.5.

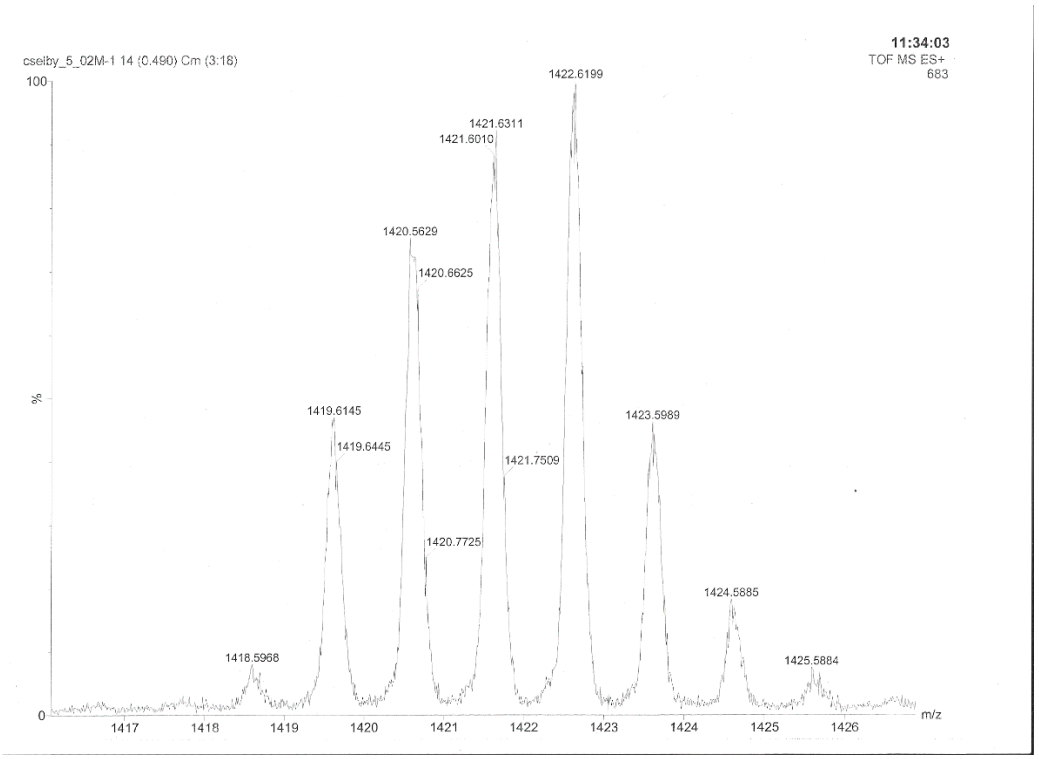

Figure 12. The ESI spectrum for organic phase 5 contacted with 0.001 M Dy in 0.2 M HNO_3 zoomed in on complex 1422.

Figures 13 and 14 show the complex peaks at 1841.7 and 1870.7 for La and 1866.8 and 1895.8 for Dy respectively. Figure 13 is zoomed in further on the complex peaks, but the difference in isotopic spread can be seen in which the La complex has much less variation, because there is only one stable isotope of La, versus the 7 stable isotopes of Dy. In the case of La, the isotopic spread is mostly due to the carbon content of the complex.

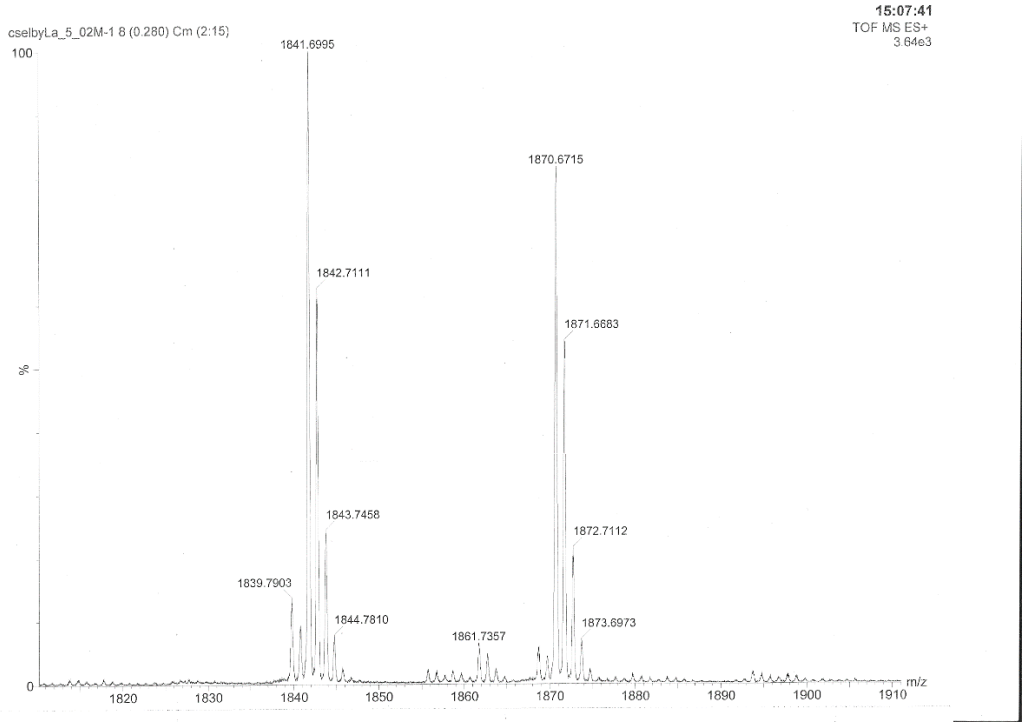

Figure 13. The ESI spectrum for organic phase 5 contacted with 0.001 M La in 0.2 M HNO_3 zoomed in on complexes.

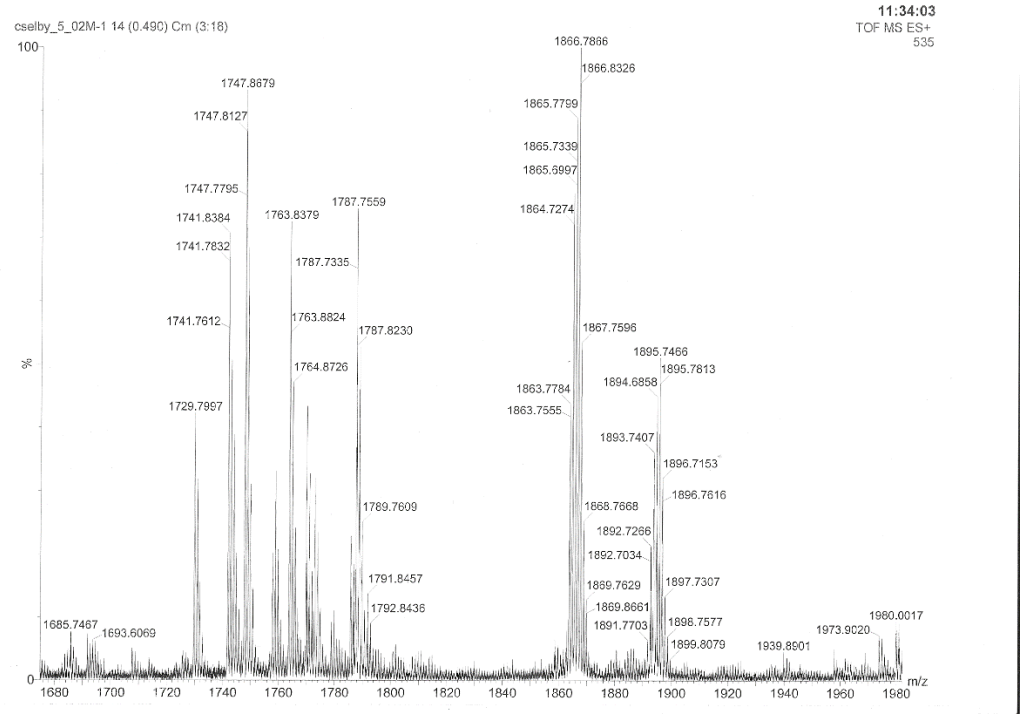

Figure 14. The ESI spectrum for organic phase 5 contacted with 0.001 M Dy in 0.2 M HNO_3 zoomed in on complexes.

Figure 15 shows the possible complex peak at mass 2322 for the extraction of Lu. This peak has a particular spread due to the isotopic abundance of Lu, which is 97.41% Lu-175 and 2.59% Lu-176, and the unknown number of carbons. Figure 16 shows the complex peaks at 2321 and 2350 where they have a much different spread than that in figure 15 due to the natural abundance of Yb, which consists of 7 stable isotopes (31.83% Yb-174, 21.83% Yb-172, 16.13% Yb-173, 14.28% Yb-171, 12.76% Yb-176, 3.04% Yb-170 and 0.13% Yb-168).

This data supports that the peaks may correspond to the same complex structure, and the spectra result in a different mass and isotopic spread because of the elemental difference between the extracted lanthanides (see Table 2 for possible complex structures).

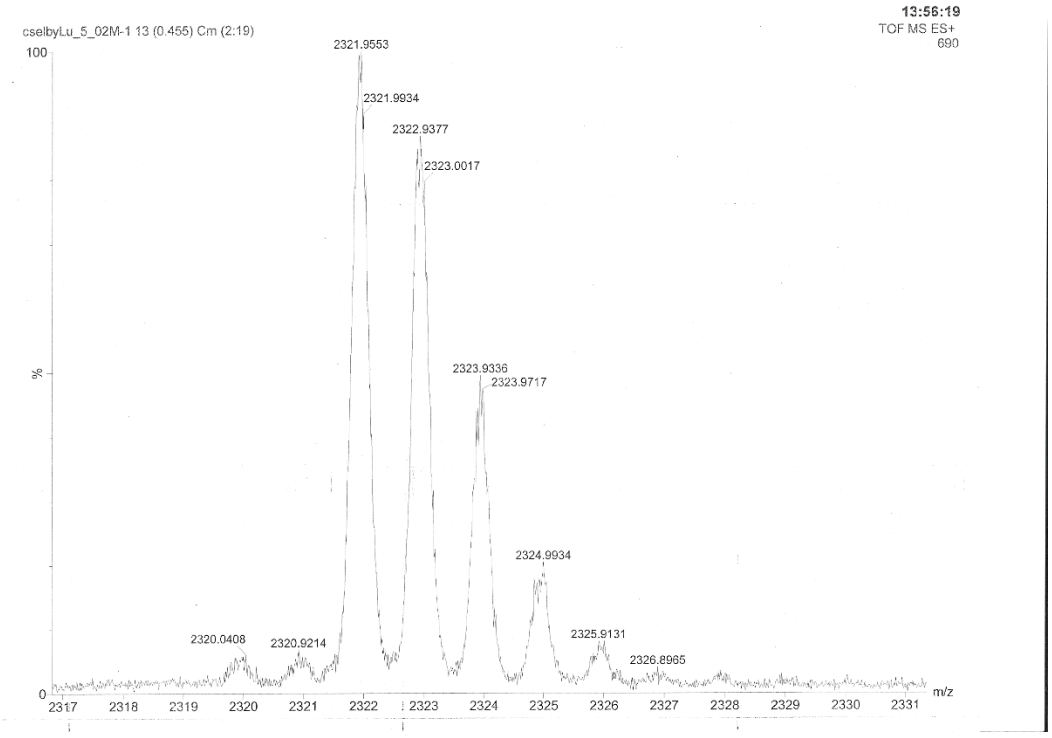

Figure 15. The ESI spectrum for organic phase 5 contacted with 0.001 M Lu in 0.2 M HNO_3 zoomed in on complex 2322.

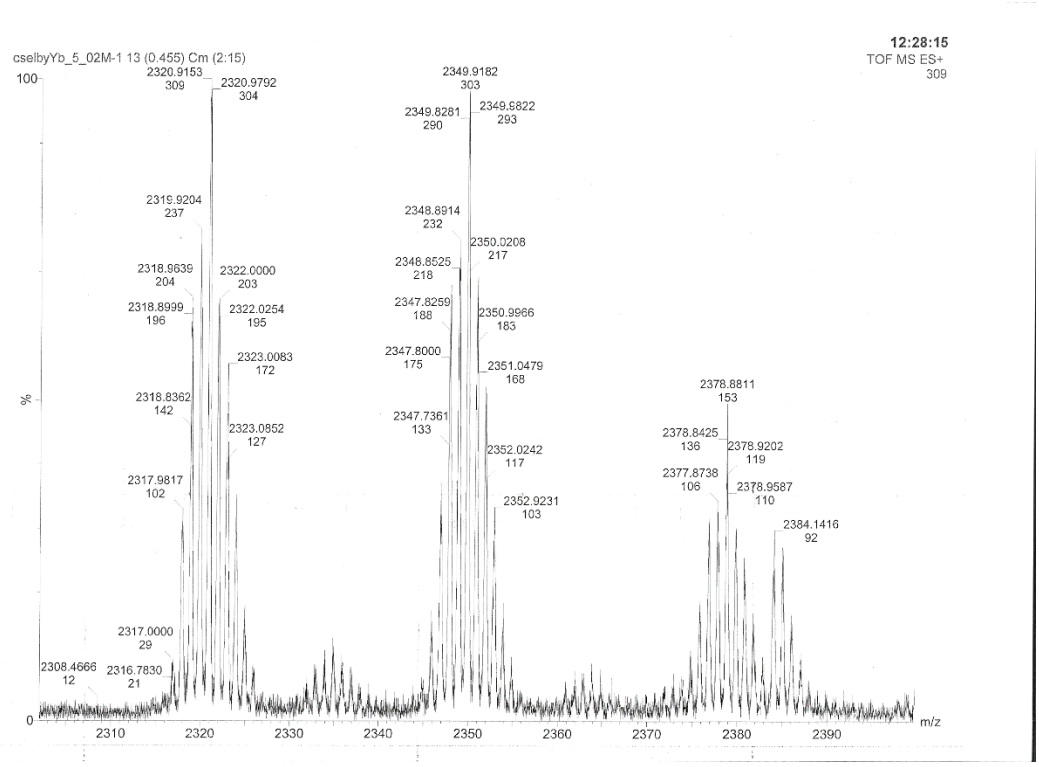

Figure 16. The ESI spectrum for organic phase 5 contacted with 0.001 M Yb in 0.2 M HNO_3 zoomed in on complexes.

Table 2. Compounds and elements used in the experiments, along with their masses were used to calculate possible complexes for the most intense peaks in the Dy extractions (1422, 1866.8, 1895.8, 2311, 2340). Example: column of Peak 1422 is calculated using 6 HDBP molecules and 1 Dy which adds to give a peak of 1423.76.

Compound or element	Mass (g/mol)	Peak 1422	Peak 1866.8	Peak 1866.8	Peak 1895.8	Peak 2311	Peak 2340
TBP	266.32						
HDBP	210.21	6	8	6	6	8	10
HDEHP	322.43						
Dy	162.5	1	1	1	1	1	1
Yb	173.04						
La	138.905						
Lu	174.97						
HNO_3	63.01		0	4	3	2	
H_2O	18.015		1	1	6		4
n-dodecane	170.335		0	1	1	2	
	TOTAL MASS	**1423.76**	**1862.195**	**1864.15**	**1891.215**	**2310.87**	**2336.66**

CONCLUSIONS

Electrospray Ionization Mass Spectroscopy (ESI-MS) is a useful analytical method in determining liquid phase compound masses, and may be useful in determining solvent extraction complexes. It has been shown to be a replicable method under different dilutions of the organic phase in the extraction of Nd with the extractant HDEHP. Also, the organic phase in this system can be kerosene or dodecane and yield nearly identical ESI-MS results. This may mean that the impact of the organic phase diluent may not influence the ESI-MS results very much.

In the extraction of Dy, La, Lu and Yb with varying amounts of TBP and HDBP it was found that a TBP only extraction yielded only one complex which may be:

$$4TBP + 2(NO_3)^- + Dy^{3+} = peak\ 1352 \quad \textbf{(11)}$$

In the mixtures of TBP and HDBP the possible complexes were also present in the HDBP only extraction meaning that the possible complex peaks contained no TBP. The intensity in the spectra of the complex peaks appears to be linked to the aqueous phase pH, in that the 0.2 M HNO_3 system yielded a lower signal than the 2 M HNO_3 system. The cause of this should be probed and is unknown at this time. Many of the possible complexes observed in the spectra of the Dy extraction were also observed in the extractions of La, Lu and Yb. There were five possible complex peaks that were much higher in signal than the other possible complex peaks and were consistent for all Lanthanides tested, and it was these criteria for focusing on the analysis of these peaks. The isotopic spread of a complex can change depending on the metal extracted in which the comparison of Dy, and Yb (containing 7 isotopes each) to La, and Lu (1, 2 isotopes respectively) yields strong supporting evidence for a peak being a complex. It can be

further supported that a peak is a metal containing complex if the mass difference between the extracted metals is also the mass difference between the peaks. The isotopic spread and mass difference of metals to mass difference of peaks analysis of ESI-MS spectra can be applied to other extraction systems and the extractions of different metals. However, as noted earlier, the dilution of the organic phase and ionization process introduce changes in the chemistry of the system analyzed. It is because of this reason that if the ESI-MS spectra analysis leads to species identification, the identification is only supporting evidence and not definitive evidence for those species existing in the extraction system. Though not definitive evidence, species identification by way of ESI-MS analysis is still powerful, and may be used to support future work, or offer motivation for particular ways of analyzing the solvent extraction system. A problem with ESI-MS analysis is that the data is specific to the chemical system. When varied, the extraction reagents and the metals extracted may yield dramatically different results on an ESI-MS spectrum.

Taking into account the results from this work with the difficulties and drawbacks of the ESI-MS method, it is evident that much work is to be done to further utilize ESI-MS in the analysis of solvent extraction chemistry. However, it has now been shown to be a step in species identification of complexes in the solvent extraction of Lanthanides with TBP and/or HDBP. The method has also shown to be replicable and it is for these reasons that the method should continually be considered in the analysis of solvent extraction chemistry.

FUTURE WORK

The next step of this work would be species identification of the complexes observed in the spectra. If the species were identified this would only apply to the extraction system tested of Lanthanides with TBP/HDBP. Although the time required to run ESI-MS experiments on these systems is minimal, the time require to analyze the spectra may be too much in many cases. This may be a disincentive for the use of ESI-MS largely because the method is not guaranteed to yield meaningful results. Therefore, the method of data analysis in this work should be streamlined, otherwise it may not be practical. Having a program help in the selection and determination of complexes would be the ideal solution. Another experiment that may yield useful data could be the ESI-MS analysis of the aqueous phase.

This work is not definitive on the subject of ESI-MS in the analysis of solvent extraction chemistry, but offers support to methods of analysis and the limitations. Due to the specificity of ESI-MS, each solvent extraction system tested may have its own set of limitations, which may not be known until the time of analysis.

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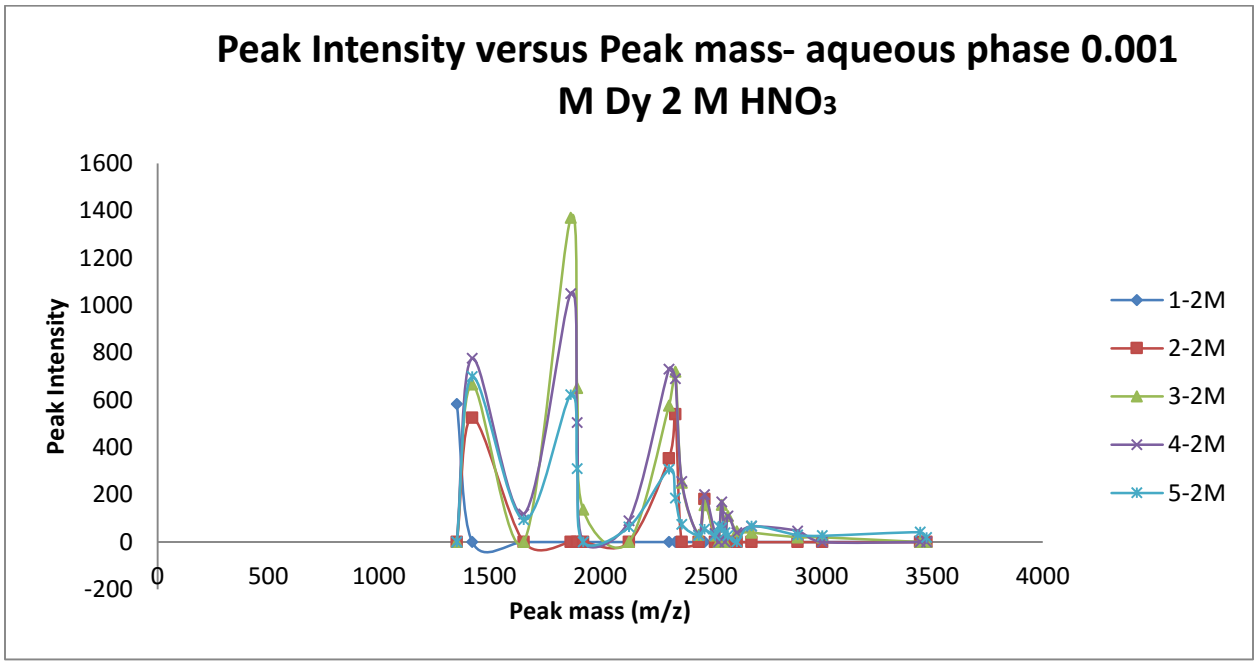
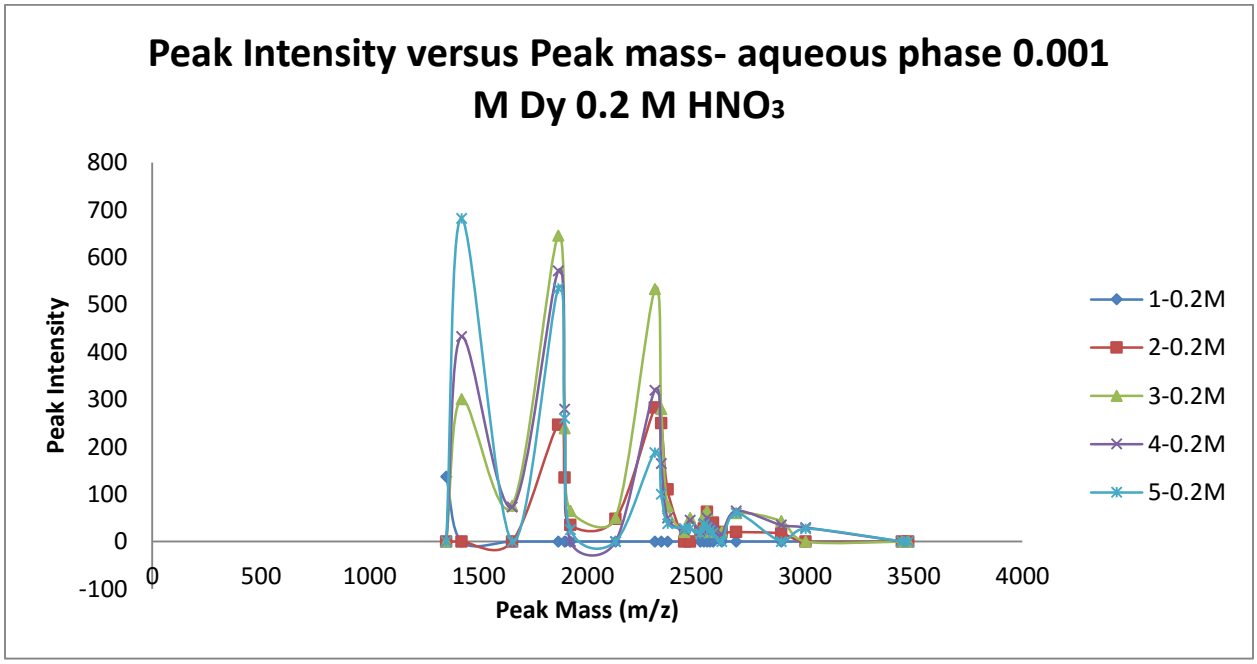
APPENDIX



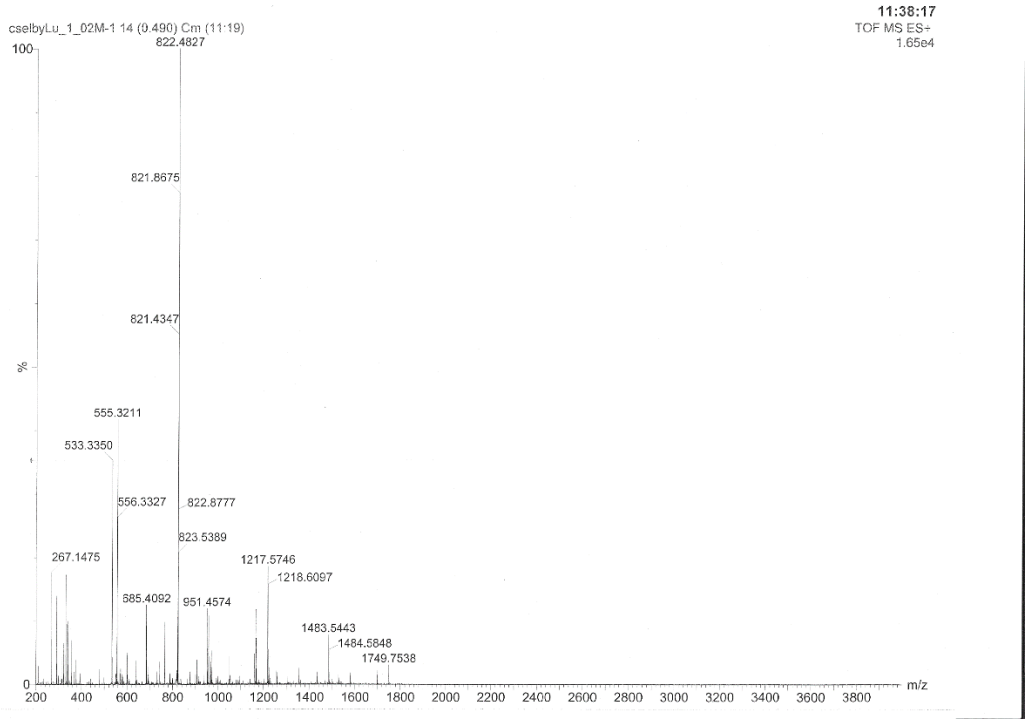
Appendix 1. The trend of peak intensity vs peak mass for the different organic phases 1-5. This is the graphical representation of the data in Table 1, only for 2 M HNO_3 aqueous phase.



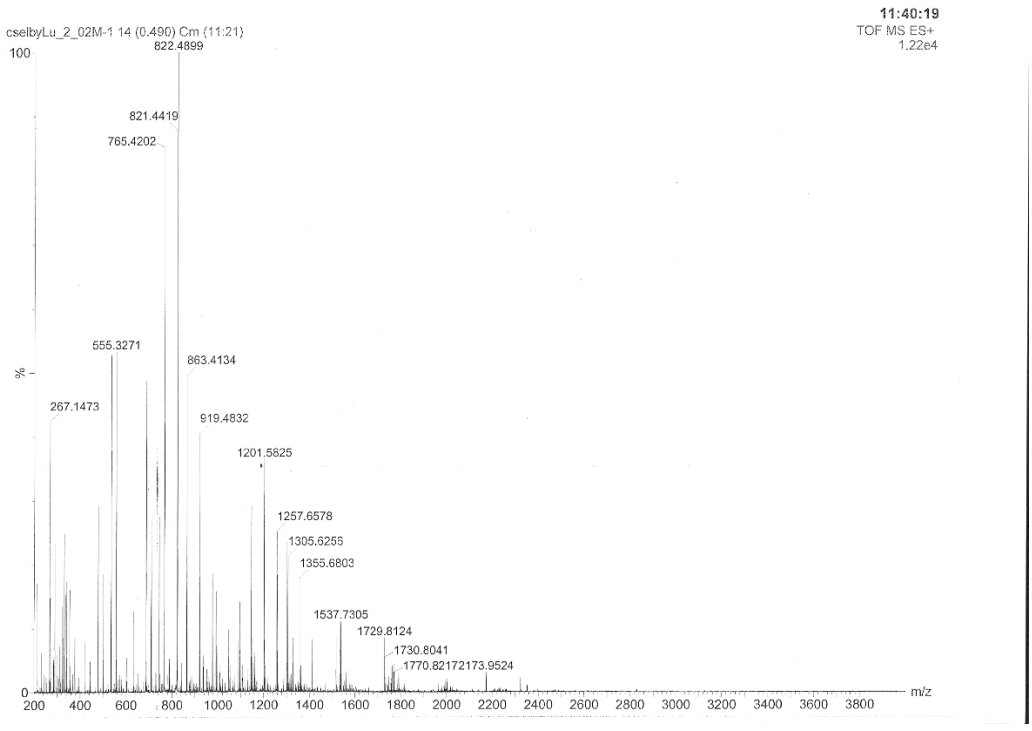
Appendix 2. The trend of peak intensity vs peak mass for the different organic phases 1-5. This is the graphical representation of the data in Table 1, only for 0.2 M HNO_3 aqueous phase.

Appendix 3. Complex peak values from the Dy spectra were mapped for other lanthanides. This was done by changing the peak mass by the difference between Dy and either La, Lu or Yb, for the replacement of 1, 2, or 3 Dy with the same number of the corresponding Lanthanide. The values under the Ln columns correspond to the masses of possible complexes that were observed, that also match the calculated masses. Blank spots on the table means those masses were not observed.

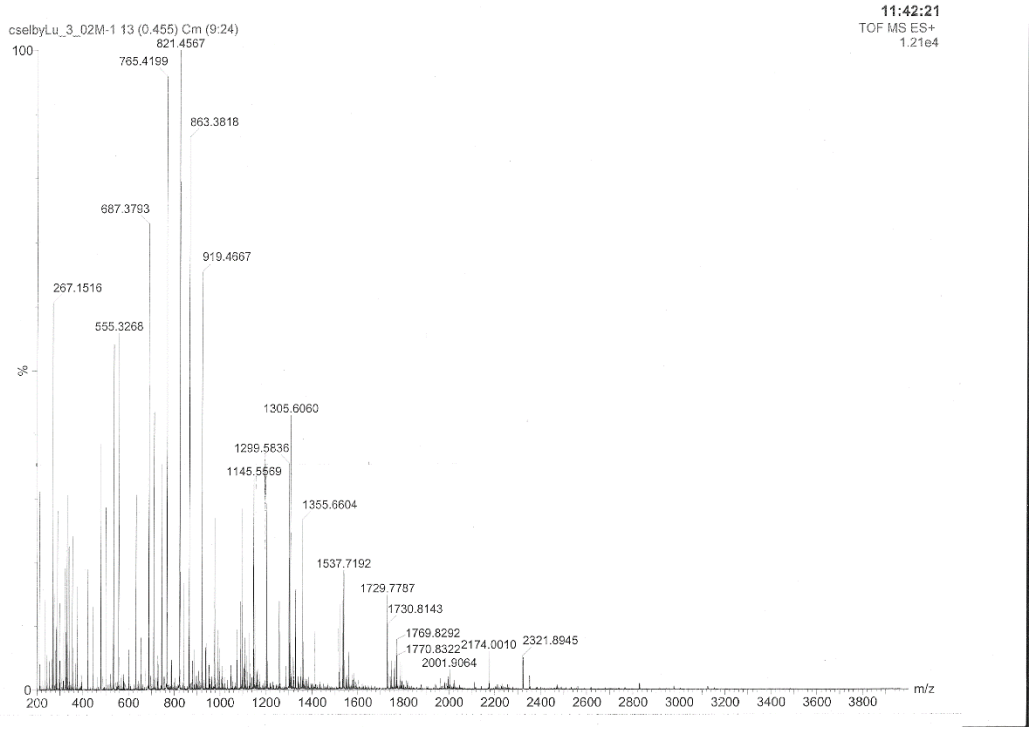
Complex Peak (Dy)	La instead	2 La instead	3 La instead	Lu instead	2 Lu instead	3 Lu instead	Yb instead	2 Yb instead	3 Yb instead
1352	1328.41			1364.47			1362.54		
1422	1398.41			1434.47			1432.54		
1654.7		1607.52		1667.17					
1866.8	1843.21			1879.27			1877.34		
1895.8	1872.21			1908.27			1906.34		
1922.8	1899.21								
2130		2082.82		2142.47					
2311		2263.82		2323.47	2335.94		2321.54		
2340	2316.41	2292.82		2352.47	2364.94		2350.54		
2369	2345.41			2381.47			2379.54		
2445.9		2398.72			2470.84				
2472									
2519	2495.41	2471.82		2531.47	2543.94		2529.54		
2535				2547.47	2559.94		2545.54		
2550	2526.41			2562.47	2574.94		2560.54		
2564				2576.47	2588.94		2574.54		
2578	2554.41			2590.47	2602.94		2588.54		
2618				2630.47					
2685		2637.82			2709.94			2706.08	
2892					2916.94			2913.08	
3004									
3447						3484.41			3478.62
3476						3513.41			3507.62



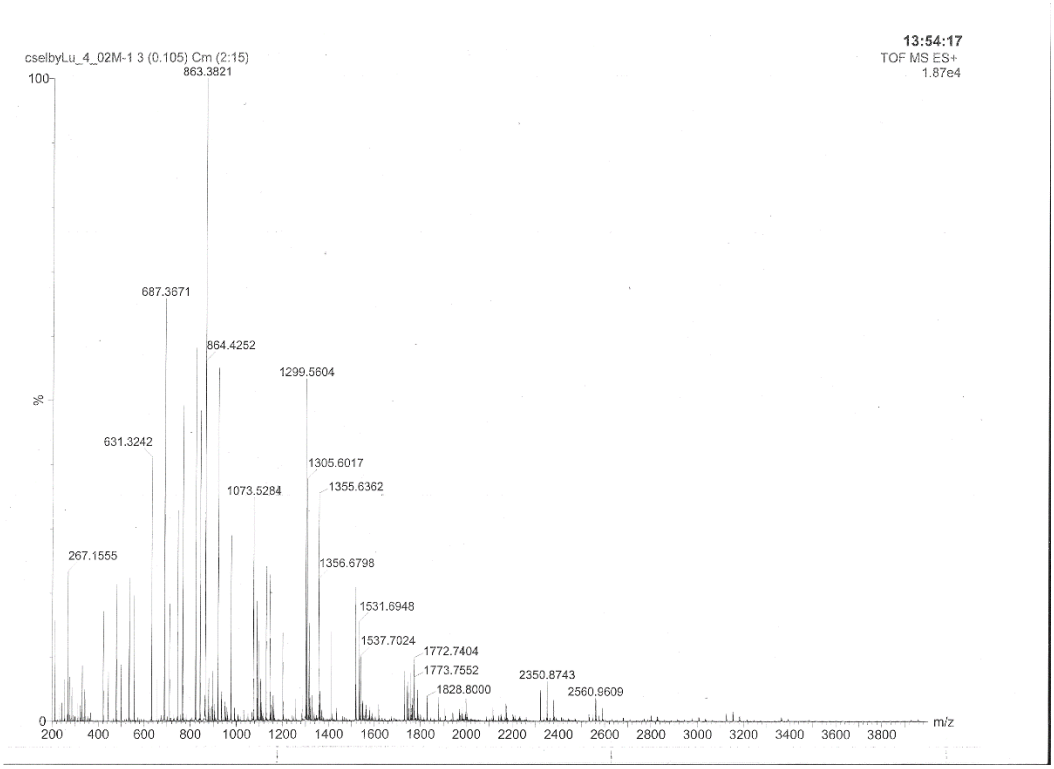
Appendix 4. The ESI spectrum from 200-4000m/z for organic phase 1 contacted with 0.001 M Lu 0.2M HNO_3.



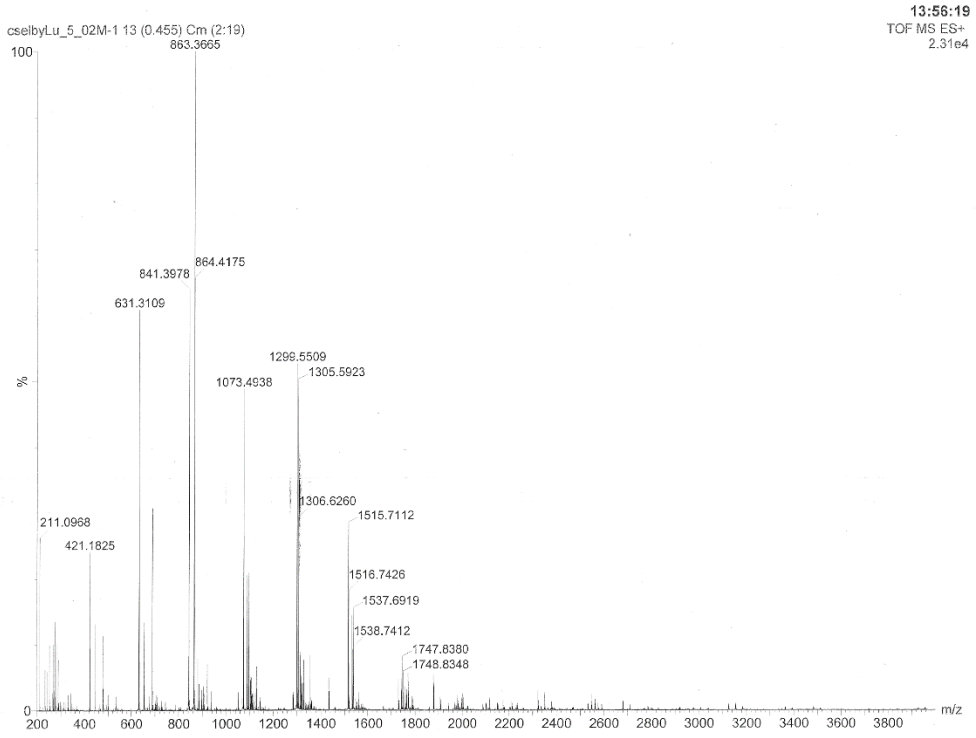
Appendix 5. The ESI spectrum from 200-4000m/z for organic phase 2 contacted with 0.001 M Lu 0.2M HNO_3.



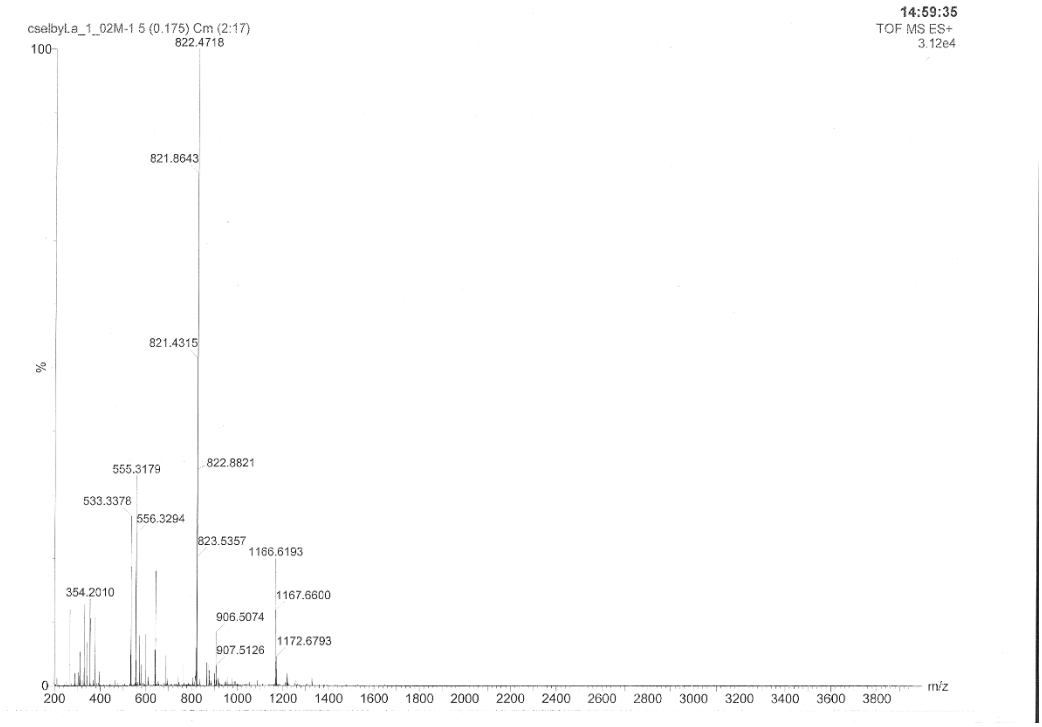
Appendix 6. The ESI spectrum from 200-4000m/z for organic phase 3 contacted with 0.001 M Lu in 0.2M HNO_3.



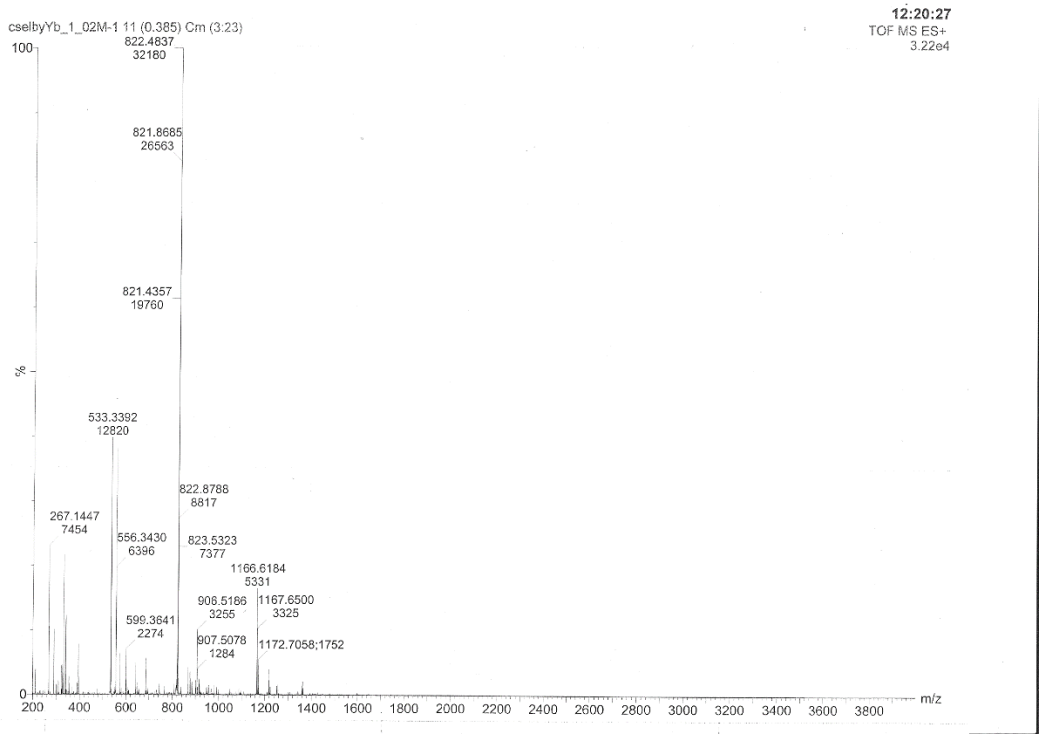
Appendix 7. The ESI spectrum from 200-4000m/z for organic phase 4 contacted with 0.001 M Lu in 0.2M HNO_3.



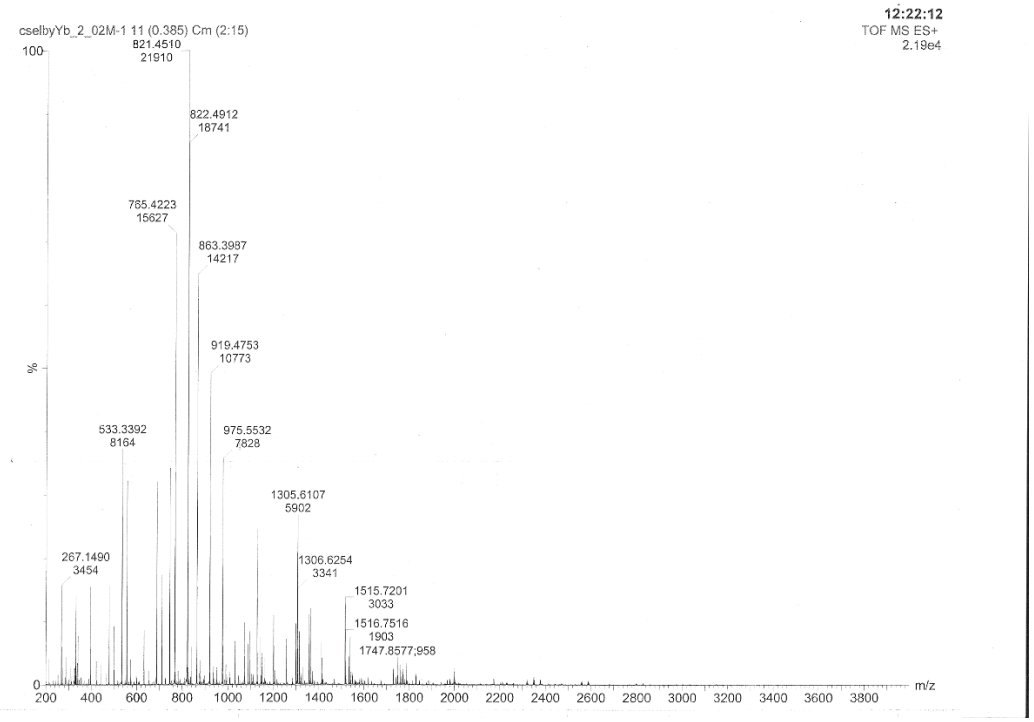
Appendix 8. The ESI spectrum from 200-4000m/z for organic phase 5 contacted with 0.001 M Lu in 0.2M HNO_3.



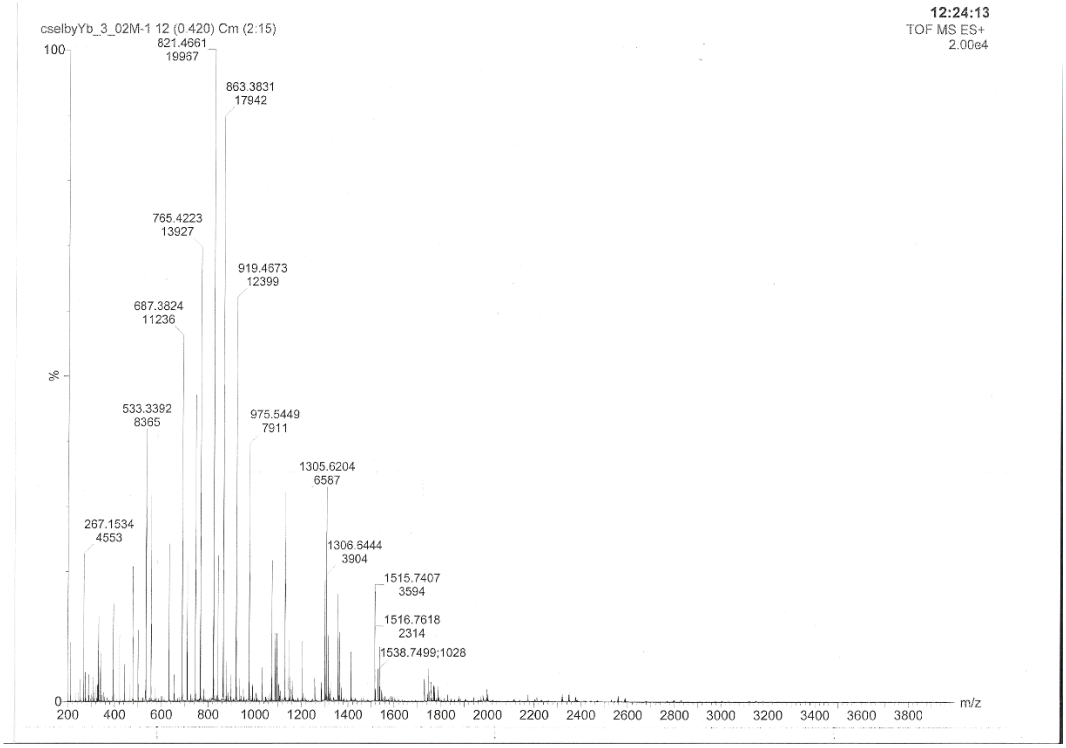
Appendix 9. The ESI spectrum from 200-4000m/z for organic phase 1 contacted with 0.001 M La in 0.2M HNO_3.



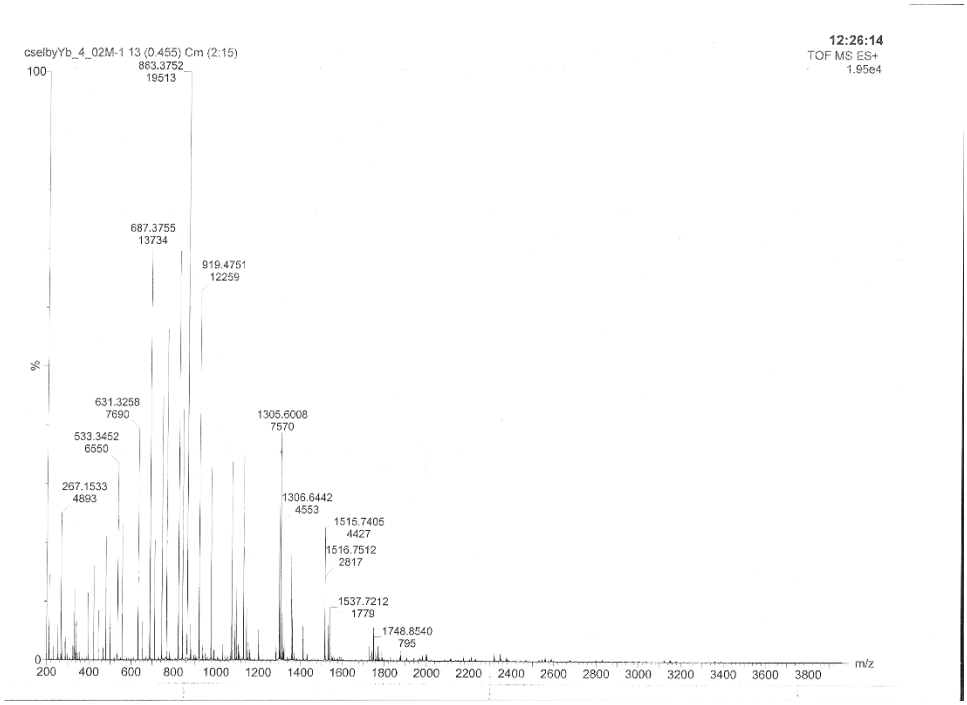
Appendix 10. The ESI spectrum from 200-4000m/z for organic phase 1 contacted with 0.001 M Yb in 0.2M HNO_3.



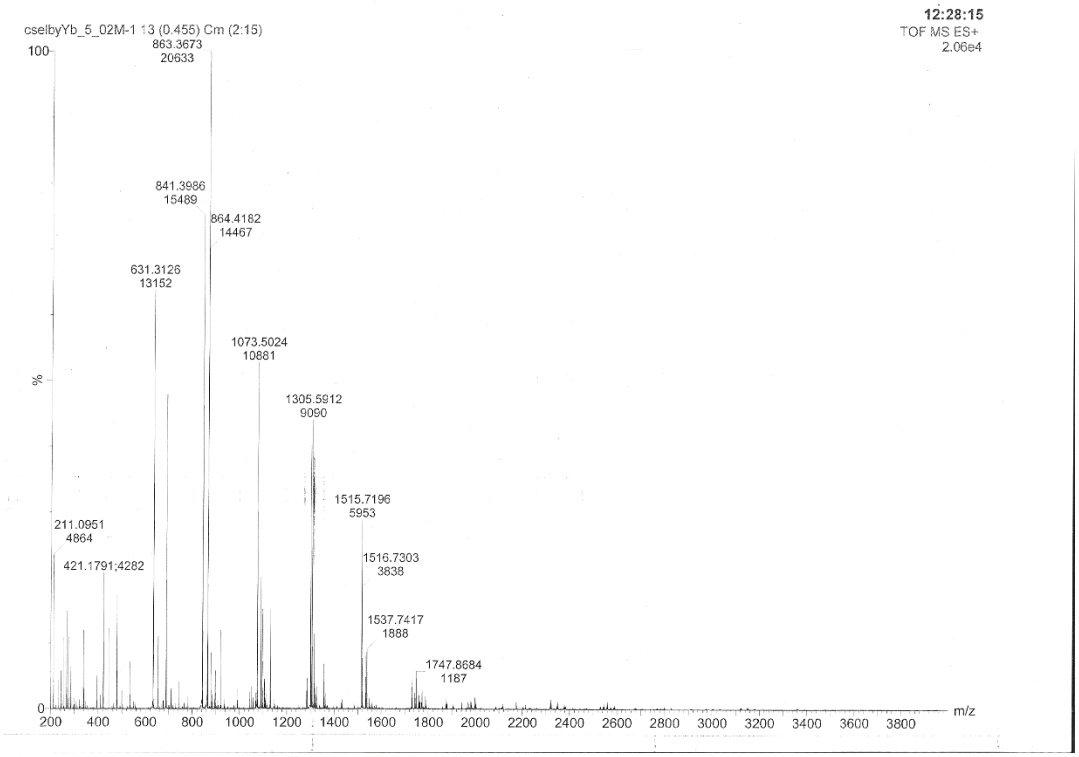
Appendix 11. The ESI spectrum from 200-4000m/z for organic phase 2 contacted with 0.001 M Yb in 0.2M HNO_3.



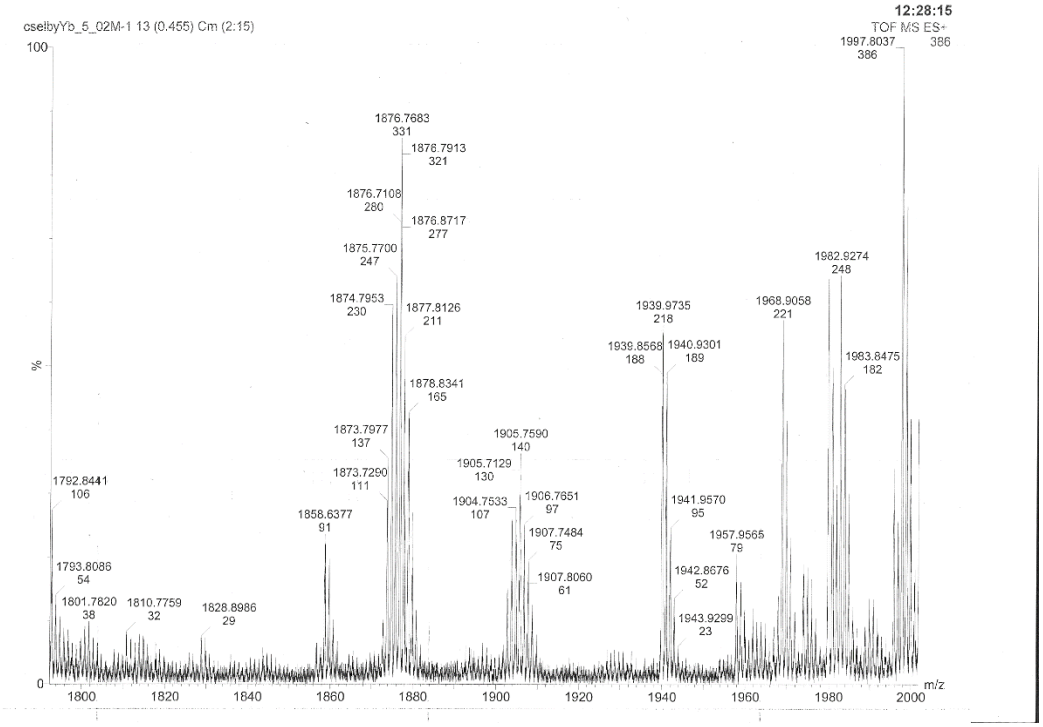
Appendix 12. The ESI spectrum from 200-4000m/z for organic phase 3 contacted with 0.001 M Yb in 0.2M HNO_3.



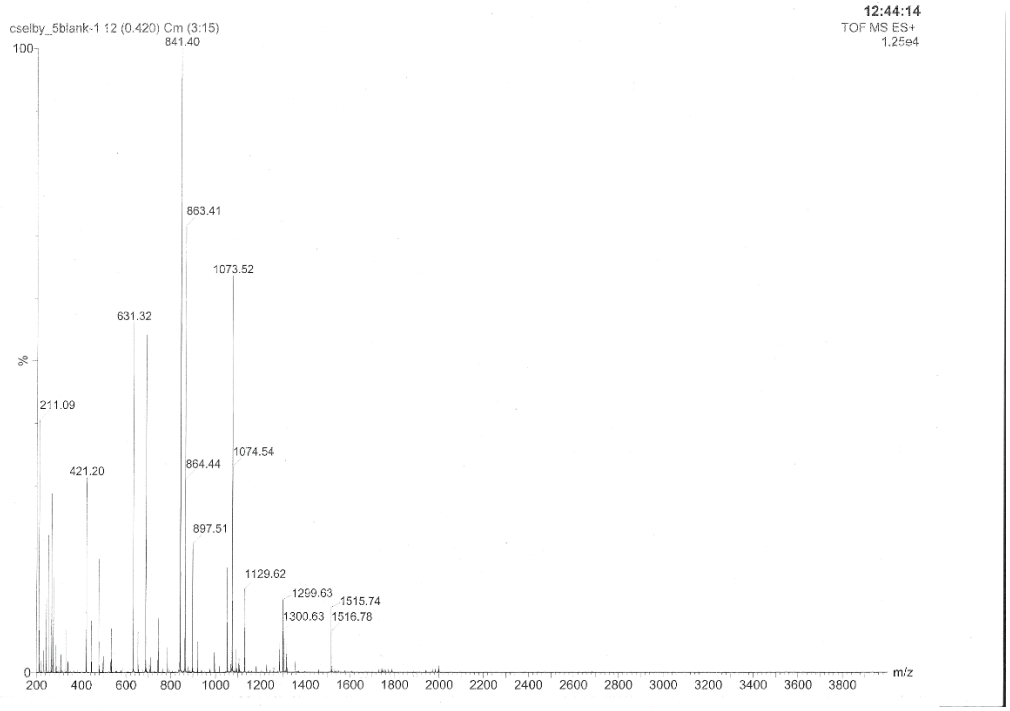
Appendix 13. The ESI spectrum from 200-4000m/z for organic phase 4 contacted with 0.001 M Yb in 0.2M HNO_3.



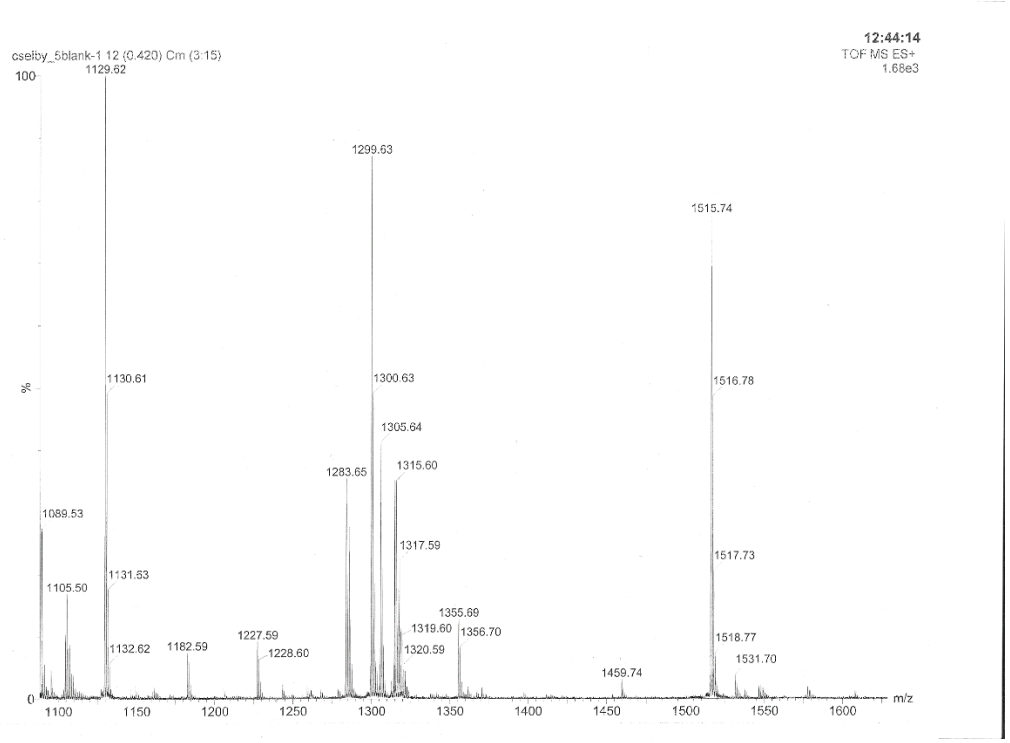
Appendix 14. The ESI spectrum from 200-4000m/z for organic phase 5 contacted with 0.001 M Yb in 0.2M HNO_3.



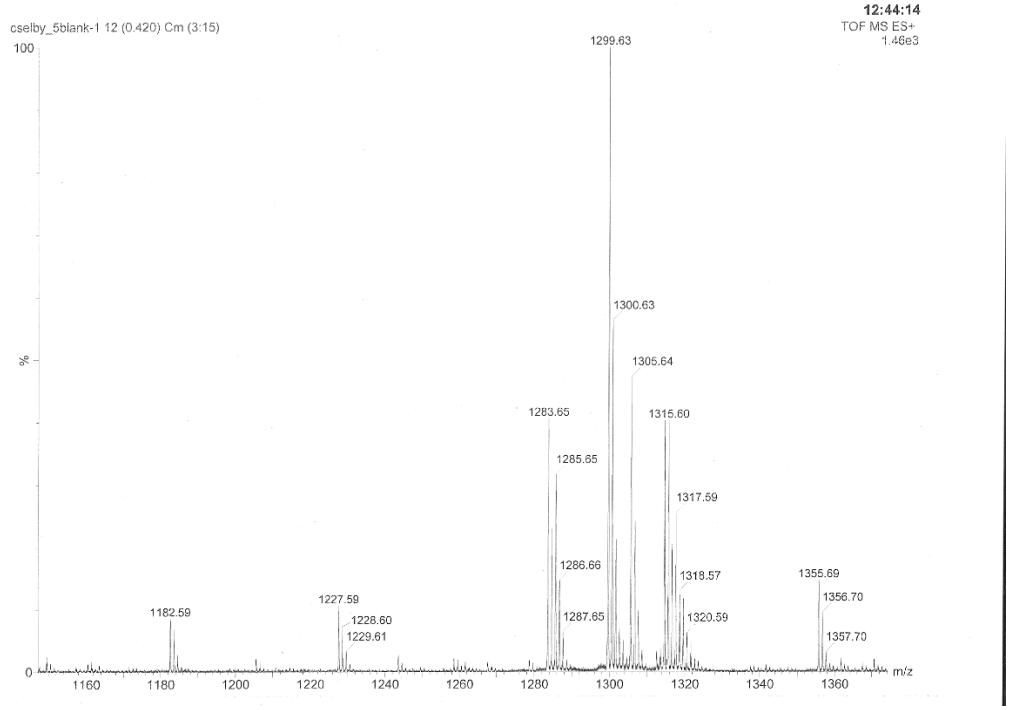
Appendix 15. The ESI spectrum for organic phase 5 contacted with 0.001 M Yb in 0.2 M HNO_3 zoomed on complexes.



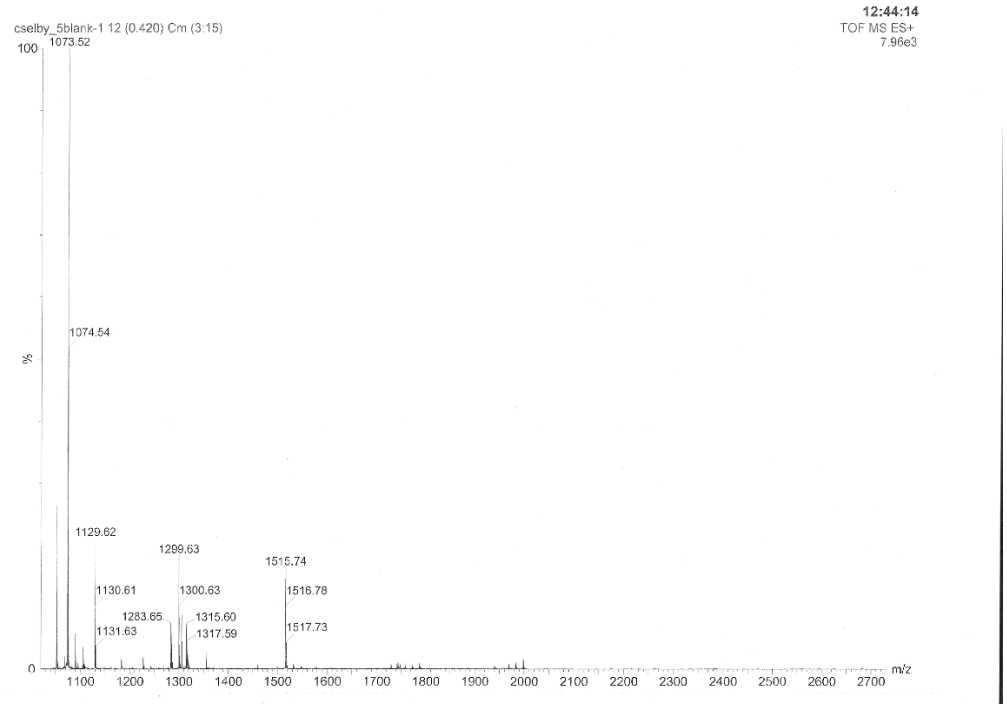
Appendix 16. The ESI spectrum for organic phase 5 contacted with non-metal loaded 0.2 M HNO_3.



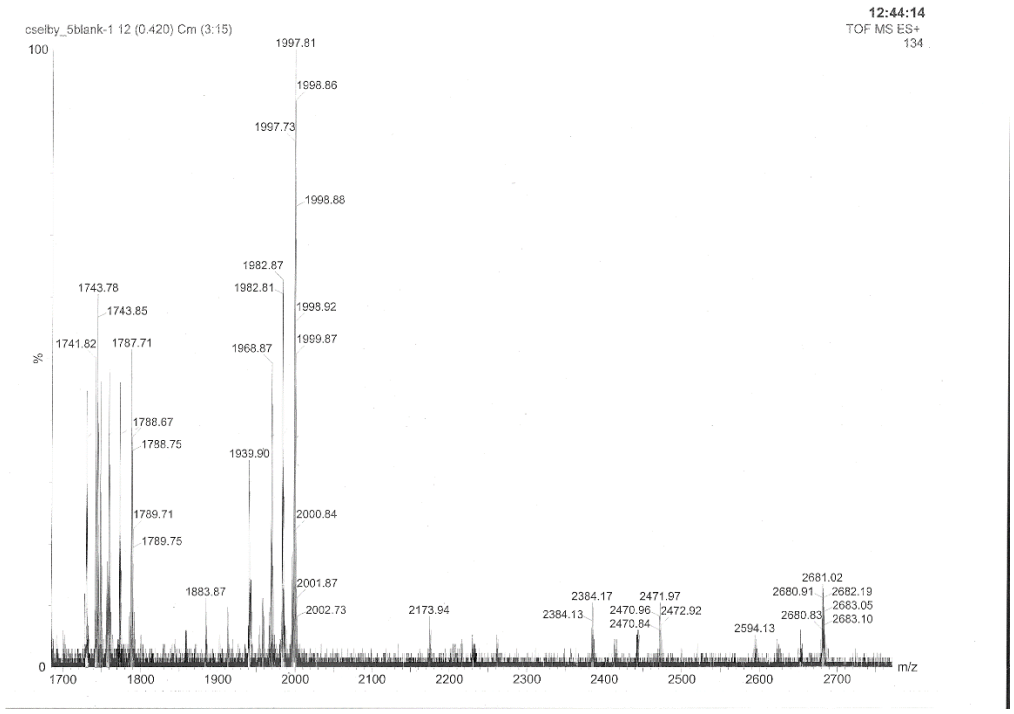
Appendix 17. The zoomed in ESI spectrum for organic phase 5 contacted with non-metal loaded 0.2 M HNO_3.



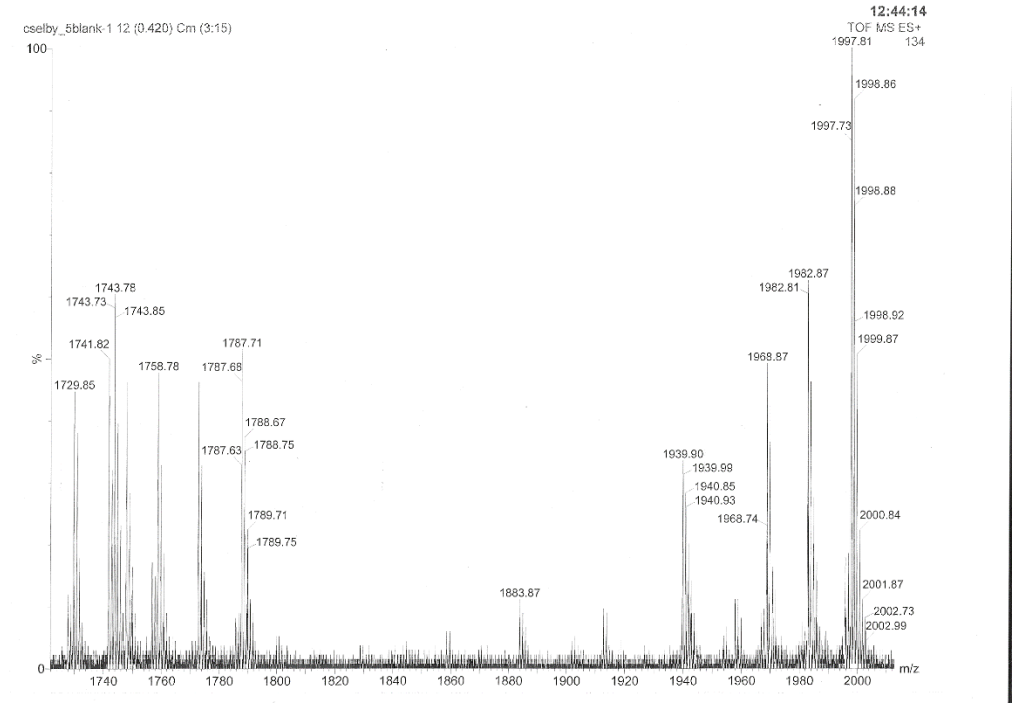
Appendix 18. The zoomed in ESI spectrum for organic phase 5 contacted with non-metal loaded 0.2 M HNO_3.



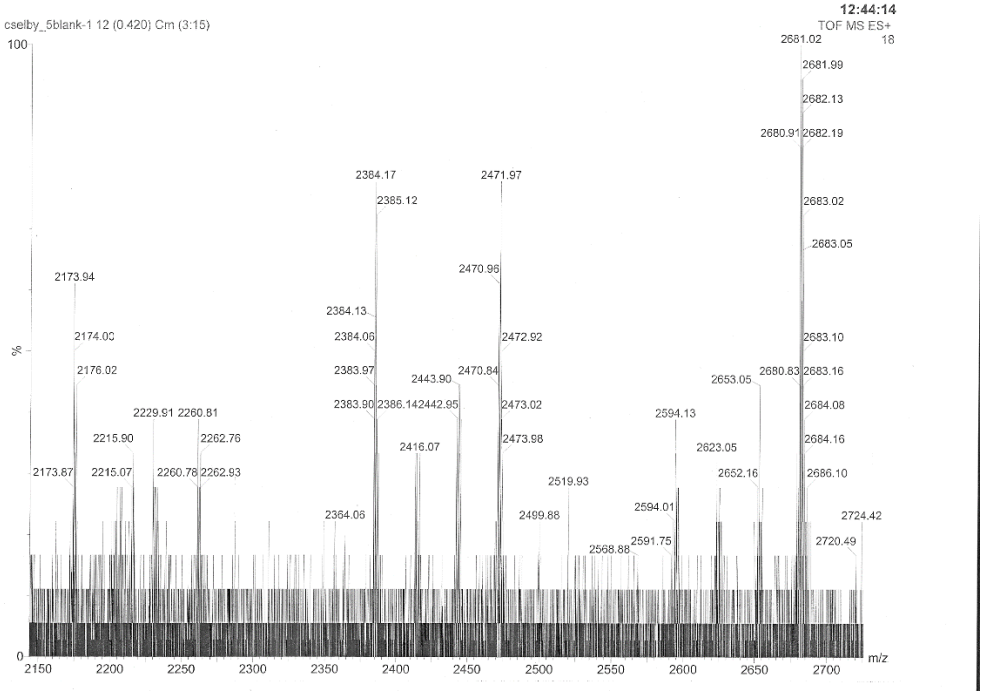
Appendix 19. The zoomed in ESI spectrum for organic phase 5 contacted with non-metal loaded 0.2 M HNO_3.



Appendix 20. The zoomed in ESI spectrum for organic phase 5 contacted with non-metal loaded 0.2 M HNO_3.



Appendix 21. The zoomed in ESI spectrum for organic phase 5 contacted with non-metal loaded 0.2 M HNO_3.



Appendix 22. The zoomed in ESI spectrum for organic phase 5 contacted with non-metal loaded 0.2 M HNO_3.