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Fast Radiochemical Separations for Neutron Deficient Short Lived Nuclides

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### Fast Radiochemical Separations for Neutron-Deficient Short-Lived Nuclides

By

Christine V. Hampton

#### A THESIS

#### Submitted to Michigan State University in partial fulfillment of the requirements for the Degree of

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#### ABSTRACT

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### FAST RADIOCHEMICAL SEPARATIONS FOR NEUTRON-DEFICIENT SHORT LIVED NUCLIDES

BY

CHRISTINE V. HAMPTON

We review both simple and exotic radiochemical techniques used for the separation, purification, and analysis of neutron-deficient short-lived nuclides. These range from classical wet-chemical methods to automated and instrumental techniques. We give special attention to chemical adjuncts of the He-jet recoil-transport technique and to high-resolution mass spectrometry. We also review recent developments in biological applications, including <sup>13</sup>N production and use. This work was commissioned for the special issue of Journal of Radioanalytical and Nuclear Chemistry commemorating the 50th anniversity of the discovery of fission.

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It is dedicated to all present and future scientists, so that we may recognise and heed the Inner Truth.

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# Chapter 1 Introduction

Exotic, short-lived nuclides have intrigued scientists ever since the discovery of radioactivity, even more so since the discovery of fission, since many primary fission products lie far from stability and have very short half-lives. A large body of radiochemical techniques has accrued over the years in connection with the study of fission products and other short-lived nuclides—an excellent library/summary of such techniques can be found in the on-going series, **The Radiochemistry of the Elements**,<sup>1</sup> produced under the auspices of the U.S. National Academy of Sciences, and in the forthcoming compilation by Rengan and Meyer.<sup>2</sup>

In general, the half-life of a radionuclide decreases rapidly the farther that nuclide lies from the line of stability. In recent years interest has increased in studying such short-lived species on two accounts: 1) Their large decay energies enable them to populate a myriad of states in their daughter nuclei, thus providing a wealth of information about nuclear structure. 2) Many applications—including those in medicine and biology—require the shortest-lived species commensurate with the experiment to minimize long-term radiation damage. Although still in use especially for the purification of radionuclides intended for medical and biological applications—straightforward wet-chemical methods have become increasingly combined with and/or supplanted by ingenious instrumental techniques. As improved cyclotrons and other accelerators enable the production of shorter- and shorter-lived activities, speed becomes an essential factor. Also, because nuclides far from stability are commonly produced by spallation/fragmentation and high-energy heavy-ion-induced reactions—inherently messy reactions, producing a wide mixture of products—it becomes important to be able to determine the A as well as the Z of a radionuclide. Thus, some type of mass identification is often combined with radiochemical techniques.

In this paper we present an overview of selected wet-chemical methods, both classical and exotic. This is not intended to be an exhaustive survey but is dictated by our own experimental experience and bias. We also review the He-jet recoil-transport (HeJRT) technique, which has been a mainstay in the clean delivery of short-lived nuclides to detector systems. We include several chemical and quasi-chemical adjuncts developed in our laboratories. Next we examine some recent methods for producing and handling 9.97-m <sup>13</sup>N, which is becoming more and more used as a biological tracer. We conclude with an examination of high-resolution mass spectroscopy as a complement to radiochemical techniques for short-lived nuclides, making a few suggestions and predictions for future developments. (As complementary reading to this paper, we recommend an earlier chapter on "Techniques for the Study of Short-Lived Nuclei."<sup>3</sup>)

# Chapter 2 . WET-CHEMICAL METHODS

#### 2.1 Overview

Sixty or seventy years ago, when the study of radioisotopes was called "isotopy" and isotopes were referred to as "atomic types," the only radioactive elements that could be obtained in weighable quantities were Th, U, and Ra. In those early days of searching for new radio-elements and developing separation methods, there occurred some discussion about whether spontaneous separation of the isotopes could be expected as a result of the gravitational field of the earth. Perhaps at higher levels in the atmosphere lighter gases might be concentrated relative to heavier ones, and perhaps various depths of the oceans might exhibit variations in isotope ratios were it not for convection currents. Centrifugal forces and biological processes were also inspected to determine whether or not they could effect separations. None was found. What became adopted as standard radiochemical separation techniques were typical analytical methods for elemental analysis, together with the radioscope (electroscope) for measuring activities. Typical examples were electrodeposition, distillation, diffusion, vaporization, photochemical reactions, precipitation, solvent extraction, and "the positive-ray method of separation" used for radio-elements that could be formed only in "invisible" quantities.<sup>4</sup>

Otto Hahn, for example, reported<sup>5</sup> that mesothorium-2 (<sup>228</sup>Ac) could be separated from mesothorium (<sup>228</sup>Ra) by two methods: by precipitating MsTh<sub>2</sub> with NH<sub>3</sub> solution and by the electrolysis of weakly-acidic solutions of MsTh<sub>1</sub> —MsTh<sub>2</sub> separates out at the cathode.

From the work of Szilard and Chalmers, Hevesy and Paneth reported<sup>4</sup> that "when an organic substance that contains I in combination with C is bombarded by neutrons, radioactive isotopes of I are produced by the capture of neutrons. The molecular binding is severed, and the radioactive I atoms are not united with C. ( $\gamma$ -ray emission breaks the chemical bond.) Because of this it is possible to obtain the active I in a very concentrated form by precipitation of the free I with Ag or by shaking up the organic liquid well with water." Thus was born the well-known Szilard-Chalmers process(es).

Differences in reaction rates were also employed for separations. By using an enzyme as catalyst and a countercurrent scrubbing apparatus, the difference in rate of  ${}^{12}CO_2$  and  ${}^{13}CO_2$  reaction with water increased the concentration of  ${}^{13}C$  from 1.06% to 1.36%.

Some gaseous mixtures could be separated by photochemical reactions. If phosgene composed mainly of  $CO^{35}Cl^{35}Cl$ ,  $CO^{35}Cl^{37}Cl$ , and  $CO^{37}Cl^{37}Cl$  was "rayed" with light filtered to the exact wavelength corresponding to an absorption line of  $CO^{35}Cl^{35}Cl$ , then that molecule was preferentially decomposed, releasing <sup>35</sup>Cl.

Even simple separations such as those of the radioactive inert gases were multistep processes. Most techniques were developed primarily for stable elements, then successfully applied to long-lived isotopes. However, as shorter-lived species were recognized and produced (primarily as intermediates in the natural decay series), faster, more sophisticated techniques were developed, often involving physical as well as chemical procedures. We present examples of a few of the most important current techniques. Some of the methods are offshoots of the original techniques, but many are much more recent developments. At times innovations in wet-chemical procedures lagged behind those in nuclear-chemistry procedures. For example, the first production of element 61 was undoubtedly made by Pool and Quill,<sup>6</sup> who bombarded Nd with neutrons, allowing the radioactive Nd isotope(s) to decay by  $\beta^-$  emission up to element 61. However, fractional crystallization was the only rare-earth separation technique available, so the activities had all decayed away before they could prove the existence of element 61 by chemical means. The first chemical proof of element 61 had to await the development of sophisticated ion-exchange separations.<sup>7</sup> In the following sections we concentrate on ion-exchange, solvent extraction (precipitation), volatilization, and thermochromatography.

#### 2.2 Separation of Actinides by Ion Exchange

One of the bulwark routine procedures for separating lanthanides and actinides is cation exchange,<sup>8</sup> which played an important role in identifying most of the heavier actinide elements. A sulfonic-acid cation-exchange resin, such as Dowex-50, is used with an ammonium  $\alpha$ -hydroxy-isobutyrate solution as the eluting agent. The smaller the charge radius, the better the complex an actinide ion forms with this reagent, so the higher-Z elements elute first from the ion-exchange column. An example of an elution curve using 0.4- $M \alpha$ -hydroxy-isobutyrate is shown in Figure 2.1. The procedure requires a heated column and a relatively slow rate of elution for the separation, so it can easily take several hours if the cleanest separations are desired. If very short half-lives are involved, however, the column can be eluted more rapidly in a non-equilibrium mode, still achieving decent separations (cf. §3.2). Because of



Figure 2.1: Elution curve of actinides from a Dowex-50 ion-exchange column using  $\alpha$ -hydroxy-isobutyrate as eluant. Taken from Ref. 8.

radiation damage to the organic solution and/or the ion-exchange resin, if "massless" sources (as for  $\alpha$  spectroscopy) are required, then the initial separation must be followed by a "clean-up" column, e.g., an anion-exchange separation using high-purity HCl as the eluting solution.

#### 2.3 Solvent Extraction Involving Very Few Atoms

Shortly after the discovery of element 103 (Lr), the question arose as to whether its most stable oxidation state was  $2^+$  like that of No or  $3^+$  like most of the other heavy actinides. Solvent extraction was used to separate 31-s  $^{256}$ Lr from other actinides and to determine its oxidation state.<sup>9</sup> The organic phase was methyl isobutyl ketone containing thenoyl trifluoroacetonate, the aqueous phase various buffered acetate solutions with *p*H values from 1.5 to 5.9.

<sup>256</sup>Lr was produced by irradiating a 250- $\mu$ -g/cm<sup>2</sup>-thick <sup>249</sup>Cf target with an  $\approx$ 70-MeV <sup>11</sup>B beam. The HeJRT technique (cf. §3) was used to transfer recoils from the reaction onto a Pt disc attached to a rabbit, which then transported it to the chemistry lab in 3 s. The Pt disc had been coated with a few- $\mu$ g/cm<sup>2</sup>-thick NH<sub>4</sub>Cl film for easy removal of the recoils. This film, containing the <sup>256</sup>Lr atoms, was dissolved with 0.1 mL of 0.1-*M* buffer solution and transferred to a 3-mL test tube containing 0.1 mL of 0.2-*M* thenoyl trifluoroacetonate solution. After  $\approx$ 10 s of agitation, the mixture was poured onto a heated Pt disc, where the aqueous phase could be pipetted off. The organic phase was dried, flamed, and counted for <sup>256</sup>Lr  $\alpha$  particles. The overall process took  $\approx$ 50 s. On average, 10 atoms were produced per experiment, but only about 1/10 this number were detected after performing the chemical separations because of decay, counting geometry, and some chemical loss. In over 200 experiments  $\approx$ 1500 <sup>256</sup>Lr atoms were produced for study. The results are shown in Figure 2.2, where various  $2^+$  and  $3^+$  species are shown for comparison. Clearly, No<sup>2+</sup> and Lr<sup>3+</sup> are the most stable oxidation states.

#### 2.4 Volatilization Techniques

Volatilization techniques have been used in many forms. Radioactive noble gases have been separated from aqueous or molten solutions by a volatilization technique sometimes referred to as "sparging," in which an inert gas is swept over or through the solution, carrying with it the volatilized radioactive gas.<sup>10</sup> RuCl has been separated from Mo, Zr, Nb, Te, and other chlorides based on differences in their volatilities.<sup>11</sup> Oxides of Tc and Re in a mixture with Ru, Os, Ir, Se, Te, and Po react with K<sub>2</sub>CrO<sub>4</sub> at 900°C, forming stable, non-volatile compounds (possibly pertechnetates and perrhenates). The other vaporized oxides do not form precipitates.<sup>11</sup>

An ion-source technique inspired by the observation of a fluoride impurity was developed at the Orsay synchrotron, using the ISOCELE-2 on-line isotope separator.<sup>12</sup> CF<sub>4</sub> is introduced as a reactive gas into the target ion source. Without CF<sub>4</sub>, a mixture of Cs, Ba, and La isotopes is produced at M/Z = 129. With CF<sub>4</sub>, volatile metallic fluoride ions are formed that undergo consecutive unimolecular decomposition of the molecular ion, MF<sup>+</sup><sub>n</sub>, to form MF<sup>+</sup><sub>n-1</sub>, MF<sup>+</sup><sub>n-2</sub>, etc. Cs forms CsF<sup>+</sup>, which decomposes to Cs<sup>+</sup>; Ba forms BaF<sup>+</sup><sub>2</sub>, which decomposes to BaF<sup>+</sup> (major component) and Ba<sup>+</sup>; and La forms LaF<sup>+</sup><sub>3</sub>, LaF<sup>+</sup><sub>2</sub> (major component), LaF<sup>+</sup>, and La<sup>+</sup>. By selecting a combination of ion-source temperature and mass, the first selective on-line separation of neutron-deficient nuclides was observed.

Researchers at OSIRIS<sup>13</sup> have also used the  $CF_4$  technique to separate Sr and Ba as monofluoro ions and Y and the lanthanides as mono- and diffuoro ions. They have also developed a technique for <sup>89,90</sup>Br and <sup>139,140</sup>I, using Al vapor introduced into the



Figure 2.2: Percent extraction into the organic phase as a function of the pH of the aqueous phase for various elements having 2<sup>+</sup> and 3<sup>+</sup> oxidation states. The plot includes points obtained for minute tracer quantities of Lr and No, demonstrating that  $No^{2+}$  and  $Lr^{3+}$  are the most stable oxidation states. Taken from Ref. 9.

ion source.

#### 2.5 Thermochromatography

On-line gas-phase separations can also be achieved using thermochromatography, which combines gas-phase reactions with thermal separations after the ion source.<sup>11</sup> This was first developed for the separation of fission products, but it shows considerable promise for fast separations of very-short-lived accelerator-produced nuclides. A carrier gas flushes the fission products from the source into a tube similar to a gas chromatographic column. The carrier gas is doped with a reactive gas that can produce volatile inorganic compounds—for example, N<sub>2</sub> with 13% CCl<sub>4</sub> produces inorganic chlorides. The column contains a combination of wall coatings for selective retention of the various compounds. By creating a falling temperature gradient across the column, groups of elements can be separated as a function of the volatilities of their compounds. <sup>11</sup> Figure 2.3 shows results for chlorides produced above 600°C with the wall coatings listed at the top and the temperature gradient represented by the slanted line. The less-volatile compounds fall on the right; more-volatile on the left.

Selective "multidimensional" separations can be made by combining two or more of the following parameters: 1) reaction with an added gas or column wall coating, 2) preferential chemisorption on the column wall, 3) low-temperature deposition of less-volatile compounds, and 4) decomposition of thermally-labile compounds at higher temperatures. An example is the separation of Ru and Tc from  $^{252}$ Cf fission products.<sup>11</sup> Tc, Ru, I, and Xe oxides were separated at 900°C with N<sub>2</sub>(10% O<sub>2</sub>) gas on an uncoated quartz column. Part of the I was retained by using an additional column coated with Ag. The Tc, Ru, and I (partial) were retained in a 150°C trap, while the more-volatile Xe compound moved through it. The trapped mixture was





flushed with HCl to form volatile Tc oxychlorides and ICl; Ru remained in the trap. Finally, the Tc and small amount of I were sent to a room-temperature trap, into which the Tc was preferentially transported by adding 2% H<sub>2</sub>O to the carrier gas. Such a procedure is an ideal one for automation.

Even greater selectivity can be obtained by combining thermochromatography with the mass-selected beam of an on-line isotope separator. At OSIRIS<sup>14</sup> a massselected beam enters the thermochromatography apparatus and is collected on a hot W filament. The separator column consists of heated concentric tubes, various segments being cooled to produce the thermal gradient. The most-volatile species leave the system through the inner tube, while other species progress through the column at differing rates. Relatively unambiguous determinations of Z can be made with this combination of techniques.

### Chapter 3

## The He-JET RECOIL-TRANSPORT TECHNIQUE

#### 3.1 Mechanism

The He-jet recoil-transport (HeJRT) technique is one of the most important methods for transporting short-lived nuclides from the target to a near or distant counting area. First developed<sup>15</sup> in the early 1960's in a quest for nuclides near the elusive doublyclosed-shell <sup>100</sup>Sn, it has undergone many modifications and improvements, but its operational mechanism is still only empirically understood.<sup>3</sup> Basically it consists of a chamber behind the target through which "doped" He flows. Reaction products recoil out of the target into the He, which thermalizes and transports them to the counting area.

There are many variants, from simple thimble-like chambers to elaborate multiple-target arrangements, from nozzles that deliver  $\alpha$  emitters directly onto detectors to long (up to 200 m) capillaries that deliver  $\gamma$  emitters to low-background areas. There are also many variants on dopants for the He and contradictory opinions as to why each works: Ultrapure He does not work, nor does the HeJRT work at room temperature in the absence of a plasma, such as produced by a cyclotron beam—for use at a reactor, an x-ray or ultraviolet source must be provided. The plasma, acting on the dopants—typically small amounts of benzene, ethylene, water vapor, even "pump oil"—produces high-molecular-weight "clusters," perhaps quasi-polymers or nucleated droplets, and these clusters pick up and transport the radioactive species. (A cryogenic variant uses pure He at very-low temperatures, perhaps creating "clusters" or droplets of a different type.)

Perhaps the HeJRT operation can be understood most easily by examining a specific set-up. Figure 3.1 shows an exploded photograph and a schematic diagram of a modular HeJRT system used at Michigan State University.<sup>16</sup> The system is attached to the end of a beam pipe at A, and the beam is collimated at B and degraded if necessary at C ("absorberdorber"). D is the target holder, and E and F are the actual HeJRT chamber—the He enters through F and exits through the 1.4-mm (inside diameter) polyethylene capillary attached to E. (G is an insulator, and H is the faraday cup.) The modular design allows for tailoring the system to a particular experiment, e.g., multiple targets and capillaries with large chambers for efficiency vs a single tiny chamber with a rear-exiting capillary for fastest transport. With this system we have been able to study  $\approx 10$ -ms activities at reasonable efficiency—at a station some 50-m distant from the target.

There have been many developments and variations on the HeJRT system, too numerous to cite here. Three of particular interest are: 1) The coupling of a gas jet with a hollow-cathode ion source for on-line isotope separation.<sup>17</sup> 2) An automated system for fast chemistry using a He + KCl jet.<sup>18</sup> 3) A "classical" HeJRT system making use of many recent improvements<sup>19</sup>—this paper also gives references to much of the recent literature.





Figure 3.1: Modular HeJRT system for delivering short-lived nuclides from the target area to a distant counting area. See text for details. Taken from Ref. 16.

#### 3.2 Wet Chemistry with the HeJRT Technique

Whatever the composition of the "clusters" in HeJRT systems, it is evident that the radioactive recoils become attached to the *surfaces* of the clusters, for the delivered activities behave chemically as simple, inorganic species and not as ions or atoms embedded inside a polymer. We used such behavior to enable us to perform very fast, non-equilibrium chemical separations.<sup>20</sup>

One example was the separation of 32-s  ${}^{63}$ Ga, 38.1-m  ${}^{63}$ Zn, and 23.0-m  ${}^{60}$ Cu, all produced by a 30-MeV *p* beam on a natural-Zn target. The set-up is shown in Figure 3.2. The flow from the HeJRT capillary was mixed (turbulently) with 8*N* HCl and directed onto the top of a Dowex-1 anion-exchange column. A large meshsize (50-100) resin was used to minimize the column hold-up time. Ge(Li)  $\gamma$ -ray detectors monitored both the column and the eluant, and we were able to improve the  ${}^{63}$ Ga/ ${}^{63}$ Zn and  ${}^{63}$ Ga/ ${}^{60}$ Zn ratios by factors of 4-10 over what was delivered initially by the HeJRT system. And this was done with the highly-non-equilibrium conditions of forcing the activities through the column in less than 1 s.

# **3.3** Cluster ("Plasma") Chemistry with the HeJRT Technique

Even faster "plasma chemistry" can be performed with a HeJRT system. This depends on the nature of particular types of clusters and is presently understood only at the most rudimentary level. Different dopants—hence, different types of clusters vary greatly in their transport efficiencies for different elements, and these differences can be used to identify and separate different radioactive nuclides. Unfortunately, the best conditions for a particular separation must be found pretty much by trial and



Figure 3.2: Set-up for performing fast (nonequilibrium) ion-exchange on activities delivered by a HeJRT system. Taken from Ref. 20.

error, for even the empirical body of data concerning these effects is meager. Nevertheless, such methods are well worth pursuing, for they are essentially instantaneous.

In Figure 3.3 we show the varying transport efficiencies for 2.20-s  ${}^{26}$ Si and 11.3s  ${}^{23}$ Mg as a function of ethylene concentration. ${}^{21}$  Both activities were produced by a 30-MeV p beam on a  ${}^{27}$ Al target. It can be seen that the transport efficiencies for both increase with increasing concentration of ethylene, leveling off around 150 ppm by volume. However, the transport efficiency for  ${}^{23}$ Mg increases more rapidly, resulting in an effective separation factor of about 12.

Cabot et al.<sup>22</sup> achieved a similar sort of effect with Hg isotopes produced by a 215-MeV <sup>40</sup>Ca beam on a <sup>144</sup>Nd target. Their results are shown in Figure 3.4. A straightforward HeJRT system transports Pt and Au isotopes quite well, but the resulting  $\alpha$  spectrum shows no peaks from Hg isotopes. However, passing some of the He over solid I<sub>2</sub> (picking up a few ppm I<sub>2</sub>) before introducing it into the HeJRT system causes peaks from short-lived (1-4 s) <sup>179-181</sup>Hg to appear.



Figure 3.3: Efficiency of transport of  $^{23}$ Mg and  $^{26}$ Si as a function of concentration of the ethylene dopant in a HeJRT system. Taken from Ref. 21.



Figure 3.4:  $\alpha$ -particle spectrum demonstrating that a small amount of I<sub>2</sub> in the He is necessary for a HeJRT system to transport Hg isotopes. Taken from Ref. 22.

### Chapter 4

# <sup>13</sup>N AS A BIOLOGICAL TRACER

Many elements important in organic and biological chemistry do not have convenient, useful radioisotopes, and until fairly recently N was listed among these. However, new fast methods of production, handling, and chemical separation have made 9.97m <sup>13</sup>N an important tracer for biological applications. From the first use of <sup>13</sup>N in autoradiography to determine the site of nitrogen fixation in blue-green algae,<sup>3</sup> this isotope has found uses in everything from studies of air pollution to "denitrification" from fertilizers by bacteria in the soil.

<sup>13</sup>N can be produced by many reactions, e.g., by bombardment of suitable targets (most often H<sub>2</sub>O) with p, <sup>3</sup>He, and <sup>12</sup>C beams.<sup>23</sup> Also, it has a far greater sensitivity than most other radioisotopes of biological importance<sup>24</sup>—it is possible to detect as little as  $3 \times 10^{-20}$  mole.

A prime example of the use of  $^{13}N$  as a biological tracer is denitrification, now being studied in many laboratories around the world.<sup>24</sup> Denitrification is the process by which nitrogen oxides, primarily  $NO_3^-$ , are reduced to gaseous nitrogen products, primarily N<sub>2</sub> and N<sub>2</sub>O, by bacteria that have the ability to use these oxides as alternative electron acceptors for their respiratory metabolism when O<sub>2</sub> is limited. Not only is denitrification wasteful of nitrate fertilizers, but also it is a considerable source of air pollution, and there has even been speculation that its products are dangerous to the earth's ozone layer. Thus, the wide interest in studying its mechanism(s) and determining ways to minimize the process.

Studies of denitrification using <sup>13</sup>N are necessarily on-line because of its short half-life. Gases such as He are used to sweep out the various <sup>13</sup>N gases produced in the bombardments, and various treatments, such as standard (Coleman) nitrogen analyzers are used to select the desired compounds. The <sup>13</sup>N compounds are then sent to soil slurries, which have been incubated with the desired bacteria, and, after the desired (short) reaction time, the products are monitored and/or analyzed. Figure 4.1 shows the results from a high-performance liquid-chromatograph analysis, contrasting the compounds removed from untreated soil vs those from soil after incubation with a culture of *Pseudomonas* bacteria.



Figure 4.1: Liquid chromatogram of the <sup>13</sup>N compounds produced in untreated soil and soil incubated with "denitrification" bacteria. Taken from Ref. 23.

### Chapter 5

## HIGH-RESOLUTION MASS SPECTROSCOPY

Of the physical techniques supplementing and at times supplanting wet-chemical methods, high-resolution mass spectroscopy is perhaps the most important. Instruments, of varying degrees of resolving power, range from classical magnetic spectrometers to electric quadrupole mass filters to recoil-product mass filters of various kinds.<sup>33,30,25</sup> In the following paragraphs we give a quick overview of the types of systems presently being used and/or under development. More details can be found in the accompanying references.

Since the time Thompson and Aston pioneered the positive-ray method of isotope separation, two differing philosophies for instrumentation design in mass spectroscopy developed—one for the analysis of stable atoms and molecules, the other for the separation of radioactive species. Both relied on determining mass through observation of the time and/or trajectory of a particle through either a magnetic (B) or electric (E) field.<sup>28,29</sup>

For radioactive atoms, visual separations were important; emphasis was placed on obtaining "weighable" quantities of an isotope. Two main types of separators evolved: In the first category, high-power ion sources were coupled with large, constant-field dispersive magnets. Initially, these isotope separators were used to analyze activities collected in an "off-line" mode. Eventually, they were placed on-line (ISOL's) with an accelerator or reactor to separate and collect radioactive nuclides produced at the target.<sup>30</sup> Many design variations in the ion source have been attempted, from  $\beta$ -decay ionization of recoils<sup>26</sup> to gas-jet-coupled systems,<sup>27</sup> with varying degrees of efficiency. The design objective was to reduce the kinetic energy and the number of charge states of the radioactive nuclides, while maintaining high currents and at least a nominal mass resolution. This increased the types of nuclides that were able to be separated by reducing the time between creation at the target and analysis. In order to separate nuclides of even shorter life times, the second main type of separator was designed that could directly analyze recoil nuclides. In the Recoil Spectrometer, counters such as  $E - \Delta E$  detector telescopes were placed after the magnetic separator stage to analyze the recoils at their original kinetic energy. This mass separation and energy analysis, combined with precision timing electronics provided two-dimensional analysis for the Z and A of an atom or ion, separated by charge states.<sup>31,28</sup> However, for exotic, large-mass radionuclides,  $E - \Delta E$  detector telescopes are not very effective. Since Q values are used to determine the mass of the fragments in nuclear reactions, any errors involved can be additive. In order to obtain higher resolution, another magnetic or electric field would have to be placed in tandem with the first.

Thompson's original mass spectrometer consisted of overlapping, perpendicularly crossed magnetic and electric fields. Grenoble's LOHENGRIN parabolic spectrometer is similar, except the E field follows the B field in a perpendicular path with the fields being parallel to each other.<sup>30,35</sup> The resulting mass resolution is 1 part in  $1.5 \times 10^4$ , with an uncertainty in the kinetic energy of the particle around 1 MeV. An example of a spectrum from LOHENGRIN is shown in Figure 5.1.

Instrumentation developed for stable isotopes in the last 10-15 years allow more



Figure 5.1: Mass spectrum taken with LOHENGRIN showing the separation of two A = 94 isobars with a resolution of  $A/\Delta A \approx 1.5 \times 10^4$ . Taken from Ref. 35.

or less routine mass determinations between  $1.5 \times 10^3$  and  $1 \times 10^6$   $M/\Delta M$ . Some of these techniques have been adapted for radioactive nuclides.

The following instruments have been developed to analyze stable isotopes: the rf quadrupole (Q), combined double-sector-field analyzers (B&E), time-of-flight (TOF), and ion cyclotron resonance with fourier-transform analysis (FT-ICR). In addition, over the past fifteen years a host of hybrid combinations of these techniques (QQQ, BEQQ, BBE, etc.) have been created. Some result in ultra-high mass-resolution analysis; others provide specialized methods for ion isolation. By coupling two or more B, E, or Q analyzers, techniques (referred to as MS/MS) have been developed for metastable ions and ions formed through collisionally-activated dissociations in order to "uncomplicate" the mass spectra, identify precursor-daughter relationships, and establish the presence of species that undergo certain decay (neutral-loss) modes.<sup>32,33</sup>

Similar techniques, such as operating the sectors at different fields, have been used in radioactive mass separators, but only as a means of deflecting contamination ions formed in unwanted charge-exchange processes occurring in the ion souce.<sup>30</sup> With the incorporation of electromagnets into ISOL design, one can convert mass separators into scanning mass spectrometers. Lampert and Chavet recently accomplished this with EMIS MEIRA.<sup>34</sup> Short-lived radioactive nuclides cannot be separated in bulk quantities; however, the MS/MS scanning techniques used for stable ions could be improved with coincidence electronics and adapted so as to enhance the presence of such radioactive nuclides relative to background.

A few speculations on the applications of these techniques to radionuclides are offered: — Ordinarily, the fragment ions from short-lived nuclides that decay within the source or first analyzer would not be focused through the second sector. When using MS/MS techniques, the second field is scanned relative to conditions in the first and, depending on the lifetimes of the nuclides, the fragment ions could be selectively focused. — If multiple detectors were used, it would be useful to focus each individual nuclide for further analysis by using a step/scan technique called "single ion monitoring". For example, this might be useful as a clean-up procedure for  $\gamma$ -ray spectroscopy. If coincidence electronics were combined with this technique, a multiple number of nuclides could be individually analyzed in one experiment. — Volatilization techniques (Chemical Ionization) could be combined with these scanning techniques in order to differentiate nuclides with the same nominal mass.

After the separation step, determination of exact mass is often necessary. The highest mass resolution can be obtained using an Ion Cyclotron Resonance Mass Spectrometer, often referred to as an Ion Trap. Mass resolution values over  $1 \times 10^6$   $M/\Delta M$  have been obtained.<sup>33</sup>

In 1981 researchers at Texas A&M University used Ion Traps with laser-fluoresence spectroscopy on line with accelerators.<sup>36</sup> As the different ions emerged from a massseparating magnet, they were trapped in flight by a quadrupole ion trap. The "Physics in Traps Panel" recently speculated<sup>37</sup> about using ion traps for high-precision mass spectroscopy of radionuclides. Radial confinement of ions in the traps is effected by a multi-kG magnetic field. The ions undergo cyclotron motion, inversely related to their masses. Fourier-transform analysis can provide a mass spectrum, reconstructed from the frequency domain. An example of such a spectrum is shown in Figure 5.2. This mass spectrum was obtained using a 4.7 Tesla superconducting magnet with a pulsed positive ion/ negative ion detection mode.<sup>33</sup> The difference in the mass of the ions is the mass of two electrons plus their binding energies.

Besides the high resolving power, there are other advantages to the Ion Trap Spectrometer: There is a signal to noise enhancement equal to the square root of the number of sampling intervals if Fourier transformation is used. High charge states do not have to be reduced. It is more appropriate to use the highest charge state possible because the signal increases linearly with charge for a given oscillation amplitude. Also, the signal coupling to the external tuned electronics circuit increases with the square of the charge.<sup>37</sup>

An Ion Trap spectrometer can be used in combination with other separators. A high-resolution mass spectrometer composed of two Penning-type traps has been in use at ISOLDE at CERN/Geneva.<sup>38</sup> The first trap acts as an ion buncher and collects the reaction products; mass analysis is then performed in the second, precision trap. Test experiments with stable <sup>133</sup>Cs indicate a mass resolving power of 1 part in  $1.1 \times 10^6$ , corresponding to a  $\Delta E$  of 0.1 MeV at M/q = 133.

An ion-guide quadrupole mass spectrometer has recently been designed that incorporates a HeJRT system to transfer recoils to a commercial residual gas analyzer, an rf quadrupole operating at ground potential.<sup>39</sup> These ions will have a kinetic energy two to three orders of magnitude lower than those emerging from a magnetic separator. The system should separate ions having half-lives as short as 1 ms. The developers suggest that it can be used as an injection stage for a high-precision mass spectrometer, such as a Penning- type ion trap.

Analyzing exotic nuclides far from stability with high resolution mass spectroscopy is just beginning. The role of Ion Traps and Fourier transformation is very promising.



Figure 5.2: Fourier-transform ion cyclotron resonance mass spectrum of  $^{35}Cl^+$  and  $^{35}Cl^-$ . Taken from Ref. 33.

# Chapter 6 SUMMARY

In this paper we have presented a quick historical overview of the development of fast chemical-separation techniques for short-lived nuclides. As improved accelerators allow the production of exotic nuclei lying very far from stability, chemical- and physical-separation techniques will grow more and more mutually dependent. Wetchemical procedures will be joined onto gas-jet transport methods, and chemistry will play a more significant role in mass separation and high-resolution mass spectroscopy. Also, radioactive tracers such as <sup>13</sup>N will play significant roles in organic and biological chemistry, necessitating development of sophisticated reaction techniques in these disciplines. Finally, the imminent widespread development of radioactive beams<sup>40</sup> should lead to even more sophisticated chemical and/or physical-instrumental procedures for dealing with ever more exotic species.

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