

Radiochemical practices

B.S.Tomar

Homi Bhabha National Institute

Lecture-16, Module-1

Hello everyone. So far, we have been discussing the fundamentals of nuclear chemistry, all the related topics related to radioactivity, nuclear structure, nuclear models, nuclear reaction, detection and measurement of different types of radiations and also producing different isotopes. Now, the remaining part of this course, the remaining five lectures or 10 modules of my portion, I'll be focusing on the applications of whatever knowledge we have gained in different branches of science, including chemistry as well as other areas. So, before that, I would just like to discuss the basic practices in a radio chemical experiment. So, we do the chemical separations, we do the radiochemical analysis, what are the practices that we need to follow that we will try to discuss in this particular lecture.



Radiochemical separations

Chemical separation of Radioisotopes/ Radioactive elements Unique resolution in Z and A

Need for radiochemical separations

1. Pure radiochemicals for applications in medicine, research, etc.
2. Radiotracers for applications in industry, healthcare, agriculture, environment, etc.
3. Study of short lived radioisotopes
4. Chemistry of heavy elements

Okay, so one of the important radio chemical practices is to do separation. Separation of radioactive isotopes we will call as radio chemical separations. Now, we can have different radio-isotopes or even in the case of actinides, you know, all the isotopes are radioactive. So, we can also call them as radioactive elements. So, we may be separating actinides or may be separating other elements but using their radio tracers.

Now, one of the important advantages of radio chemical separation vis a vis the other methods or physical methods, like in physical methods, you know, we can be using detectors. I explained the other day ΔE -E telescopes, where you can separate protons, deuterons, alpha particles and so on. The moment you go to heavier elements, you know, there is an overlapping of the signal due to different elements Z and A. And so in physical experiments, you will find it is difficult to resolve the different Z and A of the products that are formed in a nuclear reaction or even fission. In radio chemical

separation, since we are separating the elements radio chemically, and then identifying the mass number by following their decay characteristics like half-life or gamma energy. So, the resolution means in terms of neighboring elements now is unique. We can unambiguously assign the Z and A atomic number and mass number to the particular radio isotope produced in a nuclear reaction. That is what I mean by unique resolution in Z and A .

Now, what is the need for this radio chemical separation? Where do we come across? So, that is what let me just give you the brief introduction, need for radiochemical separation.

So, one is to have the requirement of pure radio chemicals. As we go along, we will see that there are many areas, particularly, when you want to use a radio isotope in medicine, particularly in diagnosis, you require a pure radiochemical, a particular tracer, like technetium-99m bound to an organic molecule, and that formulation should not contain any other chemical form. So, that is what we mean by pure radio chemicals for applications. Sometimes even in research, you may be synthesizing some particular compound, a labeled compound, and you would like to have this as pure as possible. Then we use radio tracers in many, many areas like industry, healthcare, agriculture, environmental research, and so on. And the requirement, of course, in most of the cases will be we require the radio chemically pure and also radio nuclidically pure. So, only that isotopes will be present, other isotopes should not be present, they may interfere in the experiments. So, for producing this pure radio isotopes, we require radio chemical separations.

Then we have the important area of short-lived radio isotopes. Many, many elements, particularly heavy elements, trans-actinides, whatever the discoveries are happening at the moment in the area of heavy elements, trans-actinides, half-lives are all in seconds, milliseconds, and microseconds. So, you require very nice radio chemical separation, in fact, very fast radio chemical separations, so that you can identify the Z and A of these isotopes.

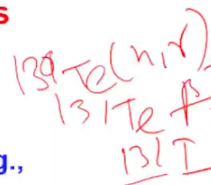
So, again, that same thing I have mentioned also, chemistry of heavy elements, you are studying the chemistry of heavy elements. From the time of nuclear reactions, their production and separation involves very fast radio chemical separation. The short-lived isotopes have also many, many applications, like for example, in PET, positron emission tomography to produce F-18 or carbon-11 or oxygen-15. They are very short-lived, some of them even seconds. And for the positron emission tomography study, after they are produced, you require them to be sent to the hospital as early as possible. So, they require the fast radio chemical separation. So, radiochemical separations have evolved a lot over the last many, many years. And I just try to give you a glimpse of that evolution. So, before we go to the different types of radio chemical separations and the applications, let

me try to give you the basic principles. The basic principles that we follow in any radio chemical separation.



Basic principles of radiochemical separations

1. **Carriers:** To minimize loss during separation e.g., during ^{131}I separation, add KI
2. **Holdback carriers:** To hold unwanted elements in raffinate, e.g., Te to prevent solvent extraction of FP ^{132}Te with ^{131}I
3. **Scavengers:** To precipitate unwanted elements a priori, e.g., $\text{Fe}(\text{OH})_3$ pptn to separate REs, Zr, etc., before Ba separation as BaSO_4 , $\text{Ba}(\text{NO}_3)_2$
4. **Separation time:** $T_{1/2}$ of radioisotope
5. **Radiochemical purity:** e.g., ^{131}I as I^- (desired) and IO_3^- (undesired)
6. **Radionuclide purity:** ^{99}Mo (desired) containing ^{93}Mo (4000y), ^{101}Mo (14.6 m)
7. **Specific activity:** Bq/g or Ci/g
8. **Radiochemical yield:** % separated in desired radiochemical form



So, whenever we are doing radio chemistry experiments, we need to take care of certain aspects and certain terminologies we use so that you know what the purpose of that particular type is. For example, we say carriers. So, in radio chemistry, radio chemical experiments, carrier actually is the stable isotopes of the element of the radio isotope. So, we are using a radio isotope as a tracer for any chemical separations. Suppose we want to trace the path of an element, or you produce a radio isotope in a chemical reaction, maybe fission or a reaction, and you have very few atoms of that particular radio isotope. So, if you want to do separation, probably you need to carry that few atoms with a bulk material. That bulk material made of the same element, but different isotope stable ones, we call as the carrier. And this carrier, in fact, are meant to minimize the loss. If you have, let us say, 1 million atoms of an isotope like iodine-131 you produce by tellurium. Suppose you have tellurium-130, which by (n, γ) reaction gives tellurium-131 and this decays by beta- to 131-iodine.

I discussed the other day in the radio isotope production. Now, this iodine-131 is carrier-free. That means only ^{131}I isotopes are there. So, if you have a Curie of ^{131}I , you may have about billions or maybe 10 billion, so 10^{10} , atoms of iodine-131. So, when you do separation in terms of the amount, 131 gram will contain Avogadro number. So, 10^{10} atoms will contain only picogram quantity. So, you cannot handle such a small quantity. In fact, when you put them in a container, many of them will get absorbed onto the wall of the container. So, minimize the loss due to adsorption or other, you know, the reagents. It's better that you use bulk, such as potassium iodide. So, you use iodide, iodine-127 to carry this ^{131}I so the losses will be minimized. Many times we require them in a high specific activity. So, you don't add bulk quantity, you may add microgram

quantity, 10^{20} atoms or 10^{18} atoms. Like that, we try because of the mass effect. So, you generate large quantity, not that large, but relatively large to avoid the loss during the radiochemical separation.

Then there is a term called holdback carriers. So, suppose along with the tellurium, you have other isotopes, for example, in fission, you have ^{131}I , you have ^{132}Te , they are fission products. Now, both of them are carrier free, means only atoms of these radioactive isotopes are present. And we want to separate ^{131}I as fission product, but we don't want to separate ^{132}Te . So, for iodine, we may use KI as a carrier, but to prevent some portion of tellurium going into along with the ^{131}I . Suppose you do precipitation, silver iodide, then there is a possibility that ^{132}Te may get adsorbed onto the precipitate. So, to prevent that absorption, or we may do solvent extraction of iodine in the carbon tetra chloride, to prevent the carry forward of tellurium in that extraction, we use some stable tellurium, telluric acid we can use, so that these isotopes of tellurium which are radioactive, they remain in the raffinate. So, that is one way of, you know, so these are the hold back, they hold the radioisotope in the place where we don't want them to carry along the separation.

And the third type of reagents are called scavengers to precipitate unwanted elements before we separate the desired element. So, we use these scavengers or the reagents to separate, to precipitate the elements which are not required to be carried forward along with them. For example, you want to separate barium as barium sulfate or barium nitrate, but along with barium, you know, many rare earths may also go, zirconium may go. So, how to prevent that they don't go along with barium. You can do a ferric hydroxide precipitation. So, you add ferric nitrate or ferric fluoride and ammonia to precipitate all the rare earths and zirconium as hydroxides. And so, now whatever is the raffinate, you add barium, the reagent sulfate or nitrate and you can separate barium in this form. So, these are called scavengers. They scavenge the undesired elements from separation along with the desired element.

So, these are mostly required for precipitation or solvent extraction or even ion exchange separation. Now, one of the important parameters for the radiochemical separation is the half-life. Half-life is very important because sometimes the half-life may be short and your time of separation may be long. So, you may lose the whole radioactive isotope. Before it is decaying, you have to separate.

Radiochemical purity is, as the name itself mentions that what is the form in which the particular isotope is present in the chemical form, that is called the radiochemical. And the purity of that radiochemical, so not only the isotope but the chemical form. So, if you want iodine as iodide, you want iodine in the form of iodide, not as iodate. So, iodine present as I^- is the radiochemical pure form desired and iodate is a different radiochemical

form which is undesired. So, you would like to produce iodine-131 as I^- , not IO_3^- in a particular application. When you need IO_3^- , then you require pure IO_3^- , I^- will be impurity.

Radionuclidic purity, as the name suggests, like molybdenum-99 is a radionuclide and you want to separate this one. But any other radionuclide, any other isotope of even molybdenum will be taken as an impurity like molybdenum-93, molybdenum-101. So, presence of them in the molybdenum-99 fraction we will call radionuclidic impurity. So, when you say radionuclidic purity is the fraction of only molybdenum-99 in the total molybdenum present in that particular consignment.

Also, the specific activity is an important parameter. You require high specific activities in some applications that you define in terms of activity per unit mass, Becquerel per gram or Curie per gram. So, depending upon the application, you may have to go for high specific activity or it may not be required at times.

And lastly, the radiochemical yield. Many times you are doing radiochemical separation, what fraction of that isotope has got separated in your final fraction. So, you started with let us say 10 curie of that particular activity and at the end you get 9 curie present that chemical form. So, we can say radiochemical yield is 90%. So, this is required to be known and for that sometimes radiotracers are also used. In radiochemical separations, radiotracers help in finding out the radiochemical yield. So, you can add a radioisotope which is not present in your sample and finally you see what percentage of this activity has been separated that will give you the yield of radiochemical separation.



Modern Periodic Table

1 H Hydrogen 1.008																	2 He Helium 4.003		
3 Li Lithium 6.94	4 Be Beryllium 9.012											5 B Boron 10.81	6 C Carbon 12.011	7 N Nitrogen 14.007	8 O Oxygen 15.999	9 F Fluorine 18.998	10 Ne Neon 20.180		
11 Na Sodium 22.990	12 Mg Magnesium 24.305											13 Al Aluminum 26.982	14 Si Silicon 28.086	15 P Phosphorus 30.974	16 S Sulfur 32.06	17 Cl Chlorine 35.45	18 Ar Argon 39.948		
19 K Potassium 39.098	20 Ca Calcium 40.078	21 Sc Scandium 44.956	22 Ti Titanium 47.88	23 V Vanadium 50.942	24 Cr Chromium 51.996	25 Mn Manganese 54.938	26 Fe Iron 55.845	27 Co Cobalt 58.933	28 Ni Nickel 58.693	29 Cu Copper 63.546	30 Zn Zinc 65.38	31 Ga Gallium 69.723	32 Ge Germanium 72.63	33 As Arsenic 74.922	34 Se Selenium 78.972	35 Br Bromine 79.904	36 Kr Krypton 83.798		
37 Rb Rubidium 85.468	38 Sr Strontium 87.62	39 Y Yttrium 88.906	40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.94	43 Tc Technetium 98.906	44 Ru Ruthenium 101.07	45 Rh Rhodium 101.07	46 Pd Palladium 106.42	47 Ag Silver 107.868	48 Cd Cadmium 112.411	49 In Indium 114.818	50 Sn Tin 118.710	51 Sb Antimony 121.757	52 Te Tellurium 127.6	53 I Iodine 126.905	54 Xe Xenon 131.29		
55 Cs Cesium 132.905	56 Ba Barium 137.327	* La Lanthanum 138.905	71 Lu Lutetium 174.967	72 Hf Hafnium 178.49	73 Ta Tantalum 180.948	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.222	78 Pt Platinum 195.084	79 Au Gold 196.967	80 Hg Mercury 200.59	81 Tl Thallium 204.38	82 Pb Lead 207.2	83 Bi Bismuth 208.980	84 Po Polonium [209]	85 At Astatine [210]	86 Rn Radon [222]	
87 Fr Francium [223]	88 Ra Radium [226]	** Ac Actinium [227]	89-102 Lr Lanthanide series [261]	103 Lr Lanthanide series [261]	104 Rf Rutherfordium [261]	105 Db Dubnium [262]	106 Sg Seaborgium [263]	107 Bh Bohrium [264]	108 Hs Hassium [265]	109 Mt Meitnerium [266]	110 Ds Darmstadtium [267]	111 Rg Roentgenium [268]	112 Cn Copernicium [269]	113 Nh Nihonium [270]	114 Fl Flerovium [271]	115 Mc Moscovium [272]	116 Lv Livermorium [273]	117 Ts Tennessine [274]	118 Og Oganesson [274]
		57 La Lanthanum 138.905	58 Ce Cerium 140.12	59 Pr Praseodymium 140.908	60 Nd Neodymium 144.24	61 Pm Promethium [145]	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.925	66 Dy Dysprosium 162.50	67 Ho Holmium 164.930	68 Er Erbium 167.255	69 Tm Thulium 168.934	70 Yb Ytterbium 173.054	71 Lu Lutetium 174.967			
		89 Ac Actinium [227]	90 Th Thorium 232.038	91 Pa Protactinium 231.036	92 U Uranium 238.029	93 Np Neptunium [237]	94 Pu Plutonium [244]	95 Am Americium [243]	96 Cm Curium [247]	97 Bk Berkelium [247]	98 Cf Californium [251]	99 Es Einsteinium [252]	100 Fm Fermium [257]	101 Md Mendelevium [258]	102 No Nobelium [259]				

Fission Products



So, radiochemical separations, most of the elements you will find there will be a requirement to do radiochemical separation at some point or other. So, for example, you are producing iron cobalt, you irradiate some targets of iron cobalt nickel and produce

some isotopes of them and you may suppose you have an alloy and you want to separate a particular isotope. You need to do radiochemical separations. For example actinides you want to separate from each other or lanthanide you want to separate from each other.

One of the classic examples of radiochemical separation when you have a large number of radio isotopes present together is fission products. You irradiate uranium with neutrons you get hundreds of fission products with half-life ranging from seconds to years. So, you have the fission product starting from let us say selenium, yield of selenium maybe 0.01 percent or so and the yield is going up reaching maximum around molybdenum and then it again goes minimum around cadmium or tin, cadmium, indium tin 0.01 percent goes up it becomes maximum around cesium barium and then finally goes down again with the rare earths.

So, all these fission products and now of course we have the high resolution gamma spectrometry set up. So, you can directly see the gamma rays of the fission products. A large number of fission products you can see together in a gamma spectrum. But earlier when we did not have the high resolution gamma spectrometers we used to do the chemistry of each element so much so that we remember the chemistry of each element how to separate. For example you want iodine immediately do solvent extraction. So, convert to iodine, do separation. You require antimony make the hydride and distil it. You require ruthenium make ruthenium tetra oxide and distil it.

So, depending upon the chemical property of that element you can find out a radiochemical separation procedure. Rare earths, they form very stable fluorides, fluoride followed by hydroxide. Two three cycles and you get pure all rare earths in one separation. So, all across the periodic table depending upon your requirement you will find you will have radiochemical separations required for these elements. The heavy elements transactinides you see here from here 104, 105, 106 most of them the chemistry is not known and their chemistry with regard to their lighter homologs are studied how they compare like rutherfordium and hafnium. So, you can use the lighter homologs as tracers to study the chemistry of heavy elements.



Methods of Radiochemical separations

Precipitation

- 1. Direct precipitation:** (i) Rare earths as Fluoride, LnF_3 , (ii) Sr and Ba as nitrates \rightarrow dissolution, scavenging $(\text{FeOH})_3 \rightarrow$ Ba separation from Sr as chromate, (iii) Ag as AgI
- 2. Oxidation state adjustment:** Ce(IV) + Zr(IV) as iodate \rightarrow reduce Ce(IV) to Ce(III) to separate from Zr(IV)
- 3. Isotopic exchange with pre-formed precipitate \rightarrow fast separation**
 - a) Cs-silico-tungstate** *PS6Cs*
 - b) Tc-tetraphenyl arsonium per chlorate $(\text{Ph})_4\text{As}(\text{ClO}_4)$** *$\text{TeO}_2$*

Now, let us discuss some of the heavy radiochemical separation procedures for example, precipitation. Precipitation also can be done in different ways one is the direct precipitation. You can take just an example I was discussing rare earths you want to separate, all of them are trivalent except cerium which can be present as Ce(IV). All others are trivalent and so these trivalent rare earths can be separated by a cycle of hydroxide followed by fluoride. So, fluoride precipitates of rare earths are clear cut. So, they are very fine low volume only zirconium may interfere and so you can do steps of fluoride and hydroxide precipitation. Zirconium will be there all around so you can do gamma spectrometry you can separate or you have to go for some complexing agents. Again they can complex one metal ion keeping in the solution form while others remain in precipitate.

So, rare earths can be separated as fluoride. Strontium, barium separations are very difficult because Strontium-90 is pure beta emitter. So, if you want to separate them you first dissolve then you first make precipitate as nitrates then you do hydroxide scavenging to precipitate out the rare earths zirconium, and other things and then you separate barium and strontium. Barium goes as barium chromate and strontium will not precipitate as strontium chromate. Similarly silver can be precipitated as silver iodide. So, there are many more examples I am just picking some of them.

Other than this direct precipitation there are cases like you can adjust the oxidation state of two elements and separate them. For example cerium and zirconium both are tetravalent and they precipitate as iodate. If you want to separate cerium from zirconium, cerium can be reduced to cerus by a suitable reducing agent and then you can separate zirconium as zirconium remains as iodate cerium comes in the solution. So, by playing with the oxidation state you can do radiochemical separation.

One of the very innovative ideas is to do isotopic exchange with a preformed precipitate. So, you do not have to add the precipitating agent afterwards and this is required when you have a very short lived isotope. For example ^{138}Cs is very short lived half-life so if you want to separate ^{138}Cs do not have much time maybe within 5 minutes you have to separate. So, you what you do, not even 5 minutes actually 1 or 2 minutes. So, you can prepare a precipitate of cesium with silico tungstic acid stable element precipitate and that solution containing cesium like fission product solution you just add shake it for a few seconds and precipitate. So, what will happen there is a stable cesium in the precipitate of cesium silico tungstate ^{138}Cs will exchange isotopically with this one in a few seconds you will find most of the ^{138}Cs has been precipitated with the cesium silico tungsten. So, you can just filter this precipitate and you get most of the cesium-138 in the precipitate. So, that is called isotopic exchange with the preformed precipitate.

Similarly for technetium, you know technetium does not have any stable isotope but perchlorate ion and TcO_4 ion are quite similar in chemistry. So, if you have perchlorate

precipitate of tetra phenyl arsenium so this is the precipitate. So, instead of technetium we use perchloric acid and precipitate this out and again this perchlorate will exchange with technetium. So, technetium-99m can be precipitated as a tetra phenyl arsonium perchlorate. So, this is like co-precipitation and very fast you can do radiochemical separation.



Solvent Extraction



Distribution coefficient (D) = C_{org}/C_{aq}

Separation factor (S) between solute a and b = D_a/D_b

Examples:

a. Fission product iodine separation: Reduce all I species to I^- using $S_2O_3^{2-}$

→ Oxidise I^- to I_2 using Br_2 → solvent extraction of I_2 into CCl_4

b. U, Pu separation: Aqueous phase = 3M HNO_3 , org phase=30% tri-n-butyl phosphate (TBP) in kerosene

Common extractants: HDEHP, TBP, TTA, TOPO, diethyl ether, MIBK, etc.



Then you have the solvent extraction. It is a very common one you will know that a metal ion let us say in aqueous phase and there is a ligand in an organic phase. So, when you mix aqueous and organic phases both liquid phases together and you shake them vigorously, because there is a potential for the metal ion to complex with ligand and which remains in the organic phase that metal will go to the aqueous-organic interface complex with ligand and then metal ligand complex stays soluble in the organic phase. You can extract the metal ion from aqueous to organic and you can then find out what is called as the distribution coefficient of metal ion into organic phase with respect to aqueous phase.

So, concentration in organic upon concentration in aqueous is called the distribution coefficient. And suppose you are separating two metal ions they will have their own D value. So, the ratio of the D value of A and B is called as the separation factor. So, you can find out separation factor for the separation of metal ions in the solvent extraction. Just to give you an example you want to separate iodine, fission product iodine.

Now, iodine is formed in many oxidation states. So, what you do you first bring all the iodine to I^- using thiosulfate as a reducing agent and now you oxidize I^- to I_2 using bromine. So, now all the iodine is now present in the molecular iodine form which can be solvent extracted into carbon tetrachloride. So, this is how you can do radiochemical separation by solvent extraction.

Similarly, uranium, plutonium you can separate them by a reagent called 30 % tri butyl phosphate (TBP) in an organic solvent like dodecane or kerosene. Aqueous phase is 3 M nitric acid and they have a very high distribution coefficient. All of them will go in the organic phase. So, there are many reagents that are used for solvent extraction such as, diethyl hexyl phosphoric acid, tri butyl phosphate, theonyl trifluoroacetone, tri-n-octyl phosphine oxide, diethyl ether, methyl isobutyl ketone. And so, there are many many reagents you know which are commonly used to do solvent extraction of metal ions from aqueous to organic phase. And later on as a function of different acidity you can strip them back in aqueous phase. So, the distribution coefficient depends upon the acidity of the aqueous phase and the concentration of the particular ligand in the organic phase. So, you have to play with the acidity to do the separation.



Ion Exchange

Partitioning of solute between stationary phase and mobile phase

Cation exchange: $RSO_3 \cdot H^+ + M^+ \leftrightarrow RSO_3 \cdot M^+ + H^+$

Anion Exchange: $R_4N^+Cl^- + X^- \leftrightarrow R_4N^+X^- + Cl^-$

Example:

Separation of Th from U: Dowex 1x8 anion exchange resin + U, Th in 6-8 M HCl, U as $UO_2Cl_4^{2-}$, Th as $ThCl_4$ → U is held up, Th is not.

Separation of individual rare earths: Dowex 50x4 cation exchange resin + RE in 0.1 M HCl → REE are held up on column → elution with α -hydroxy isobutyric acid → Lu elutes first, La at last

Similarly, ion exchange resin, ion exchangers are very common reagents for separation of different species. So, again it is based on the partitioning of the solute between a stationary phase that is the resin and a mobile phase. Mobile phase could be acid or it can be a base or it can be containing complex agent. You can have resins based on cation exchange or anion exchange. So, like for example, you have a polymeric base styrene or divinyl benzene on which you have anchored the functional groups like sulfonate and you have the H^+ .

So, it is a neutral species, but the H^+ is exchangeable. So, the metal ion in the mobile phase can exchange with the H^+ and the metal ion will be retained in the resin, H^+ will be released. In the case of anion exchange resin, the quaternary ammonium salts containing chloride as a counter ion are exchanging that. So, you can have the anions exchanging with chloride and you have the anion retained in the column, chloride being released. So, you can have this ion exchange from different acidic media, HCl, HNO_3 , $HClO_4$, H_2SO_4

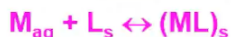
and so on. But the important thing is that depending upon the ionic potential, metal ions are retained by the resin and then you can do separation.

Just for example, you want to separate thorium from uranium. So, you can have anion exchange resin, Dowex 1x8, keep all uranium thorium in 6 to 8 molar HCl, wherein uranium forms anionic species, but thorium does not form anionic species. So, in the anion exchange resin, uranium will be held up, whereas thorium will not be held up. So, you can just wash the column, all thorium comes in the effluent and you can later on elute uranium by using a dilute acid.

Similarly, the individual rare earths can be separated using a Dowex 50x4 cation exchange resin. You take all of them in 0.1 molar HCl, so dilute acid. Since H^+ is not competing, all the rare earths will be held up in the column. And now you want to elute them individually. So, there is a beautiful reagent called alpha hydroxy isobutyric acid, which will complex these different rare earths. And since the stability constants are different for different rare earths, you will find, because of the rare earth ions having different ionic potential, hence different stability constant by eluting with this particular reagent, individual rare earths will come one by one. The one, the lowest ionic radius, lutetium will come first and the lanthanum will be the last.



Extraction chromatography



Stationary phase: Complexing agent sorbed on inert support

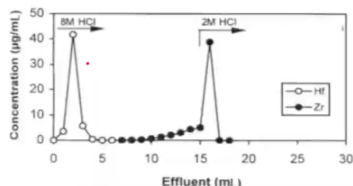
Mobile phase: H^+ , OH^- , etc.

Examples

Separation of Zr and Hf using ^{95}Zr and ^{181}Hf as tracers

Extraction chromatography column: tri-caprylyl monomethyl ammonium chloride (Aliquat 336) on styrene / divinyl benzene

Elution with 8M HCl (Hf) and 2M HCl (Zr)

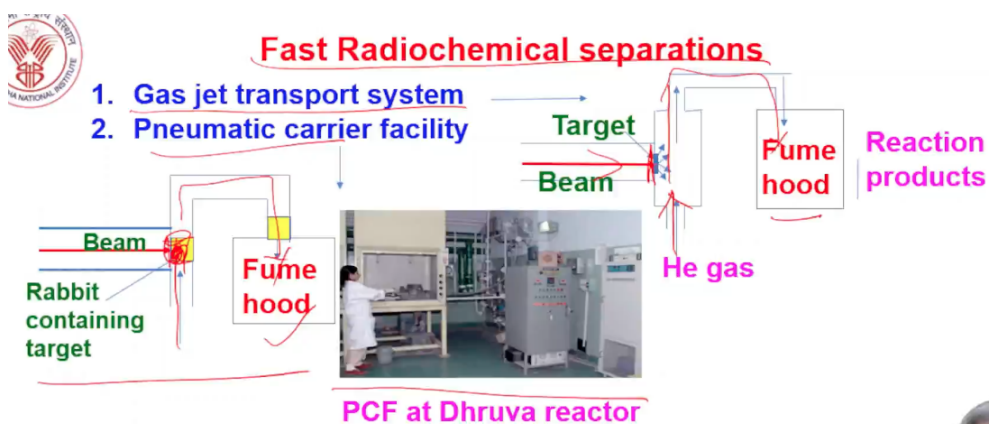


Journal of Chromatographic Science, 37, 171 (1999)

Another, just similar to ion exchange resin, you have extraction chromatography. So, here the ligand actually is on the solid surface. So, you have a solid surface, stationary phase, solid phase, and some ligand, adsorbed onto an inert support that form the stationary phase and the mobile phase will contain the metal ions in the presence of H^+ , OH^- and so on. So, you have a solution containing metal ion and you have a ligand adsorbed onto the solid support. If you pass the solution of metal ion through this column, the metal ion will

complex with the ligand and get retained by the column and later on, you can elute that one.

Just to give an example of very careful separation of zirconium, hafnium. Zirconium, hafnium are chemically very similar because of their similar ionic radii and being in the same group, you can separate them using extraction chromatography. This is one example, the tricaprilyl monomethyl ammonium chloride called Aliquat-336 is an extractant adsorbed onto this solid support. And then you first load it from a dilute acid, elute hafnium with 8 molar HCl and zirconium with 2 molar HCl. So, you can see here this I have taken from this paper that zirconium and hafnium are very well separated. This is hafnium, this is zirconium. So well separated are the peaks due to two metal ions in this extraction chromatography system.



Fast chemistry

- a) Hydride volatilization (Sb, Sn, Te)
- b) Isotopic exchange with preformed precipitate
- c) Solvent extraction
- d) Proton irradiations in air



Now, lastly, let us discuss the fast radiochemical separations. Many a times the half-lives are very short, seconds, milliseconds and so on to even you know less than a minute is a very you require very fast chemistry. And so there are techniques like gas jet transport system.

The gas jet transport system what you do, you have a beam. So, you are doing experiment in the accelerator. The beam is going here, you have a target here. Now, target is thin enough when the beam falls on target, the products are found in this chamber and the helium gas is passed through this chamber. The helium gas will transport all of the reaction products to the fume hood in your laboratory. So, you have a pneumatic system and all the reaction products will go in the fume hood, you can collect the products in a solution to do the chemistry. So, the transport time for the reaction products from the

reactor or accelerator to the fume hood becomes a few seconds, one or two seconds. And then the chemistry also you have very fast chemistry apparatus you can do.

Other one is the pneumatic carrier facility. The pneumatic carrier means this is the rabbit, you have a rabbit capsule, this capsule, the target is not fixed in the chamber, but you have the target fixed in the rabbit or capsule. This is contained the target like in a reactor. So, this is a reactor and neutrons are everywhere. You have a pneumatic tube through which you take the capsule here, irradiate for some time and later on carry to the fumehood. So, you have to break open the capsule and the target is present in the capsule, you can separate the reaction products from the target. So, while you have only the reaction products in gas jet transport system, in pneumatic carrier facility you have the target also. So, this is a typical pneumatic carrier facility in the Dhruva reactor, my colleagues have built, where you can carry the rabbit in the fume hood and do the chemistry.

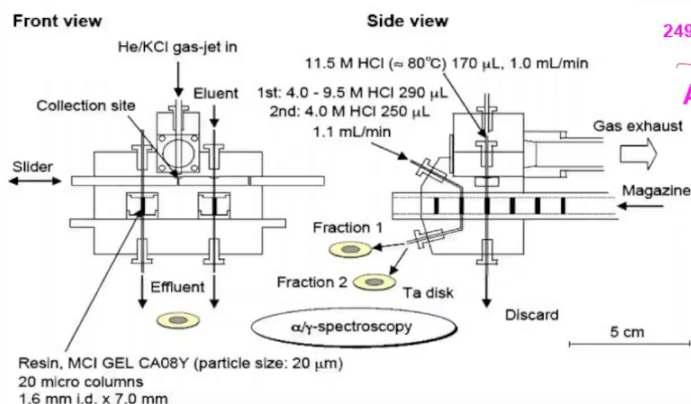
So, some of the examples of fast chemistry like antimony, tin, tellurium, which can form hydrides within a few seconds you can separate them, isotopic exchange with a pre-formed precipitate, solvent extraction, in accelerators for proton beams you can irradiate in the air.



Automated Rapid Chemistry Apparatus (ARCA) Chemistry of elements 104, 105, 106

Gas – jet transport → HPLC

N. Trautmann *Radiochimica Acta*
70/71, 237 (1995)



$^{249}\text{Bk}(^{16}\text{O},5n)^{262}\text{Db } T_{1/2}=34\text{s}$

Atom at a time Chemistry



Similarly, for heavy elements, you can do rapid chemistry automated rapid chemistry apparatus to have a gas jet transport system followed by the high performance liquid chromatography. And one of the elements like, you know, the Dubnium-105 was separated by this ARCA system using a gas jet system and you can switch between different columns to do separation of different elements. So, atom at a time chemistry means at a time only one atom is formed. So, you do thousands of chemistries to do the separation large number of times and then that is how you study the chemistry of this

element. So, thermodynamic quantities of heavy elements are determined by doing chemistry 1000 times where you have at a time only one atom.



PET Radiochemical separation units

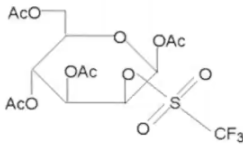


Fast radiochemical separation unit

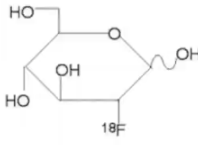
Nucleophilic substitution of F-18

Precursor: Mannose triflate

Catalyst Kryptofix



Mannose triflate



^{18}F -FDG

S. Yu, *Biomedical Imaging and Intervention Journal*, 57, 2006



And lastly, you have the PET, Positron Emission Tomography, you require a short-lived positron emitters like fluorine 18, carbon 11 and so on. So, you have to have very fast radiochemical separations because the half-lives are very short. So, like for example, F-18 from H_2O you have H_2O , you irradiate H_2O^{18} with the proton beam and then you separate F-18 from this irradiated water using a particular precursor and the catalyst.

So, this is the reaction given to prepare this F-18 labelled FDG. Then you have to have a fast radiochemical separation where within few minutes the whole F-18 labeled with the glucose molecule is separated from the irradiated target. that is H_2O^{18} . So, the whole module, whole system is a very compact form and you can supply the radiochemically pure and sterile sample to the hospitals in a very reasonable frame of time, may be few minutes time you can do this. So, I will stop here. Next, I will take the radioanalytical techniques and their applications. Thank you very much. Thank you.