

PART V

Counting Radioactive Samples

Outline

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4. Chromatography
5. Distillation and Volatilization

C. Sample Preparation

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II. Counting Efficiency

A. Detector Efficiency

1. Counting Efficiency
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4. Backscattering
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III. Problems

SECTION I

Preparation of Counting Samples

A. Purification - implies separation by analytical techniques of desired radionuclide from other contaminating radioactivities.

i) Choice of separation techniques depends on:

1. Tolerance level for radioactive impurities
2. Selectivity for the desired radionuclide
3. Speed
4. Volumes involved.

ii) Concentration of typical tracer level solution:

Ex: 1 ml of ^{60}Co solution (10^3 disintegrations/sec/ml)

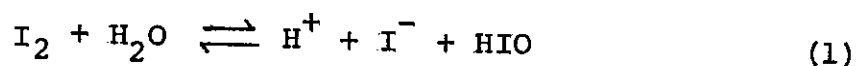
$$A = \lambda N = 10^3$$

$$N = 2.4 \times 10^{11} \text{ atoms/ml}$$

$$\text{concentration} = 4 \times 10^{-10} \text{ molar}$$

iii) Important problems due to LOW CONCENTRATION EFFECTS:

1. Adsorption of radioactive atoms on dust particles, vessel walls, pipets, etc.
2. Shift of chemical equilibrium, e.g.,



3. Differences in rates and mechanisms of reactions

iv) These problems may be avoided by adding a macro amount of:

1. isotopic carrier (stable isotope of the element being purified)
2. hold back carrier (stable isotope of the impurity)

B. Separation Techniques

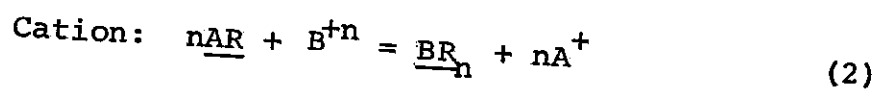
1. Precipitation - can be used to isolate desired radionuclide or to remove undesirable contamination. Technique requires the use of isotopic or hold back carriers.

Rules for maximum results:

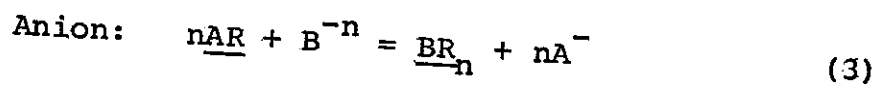
- a. slowly add relatively dilute reagent solutions to a hot solution of the radioactive sample
- b. if necessary to avoid hydrolysis, adjust pH of reagent
- c. digest solution by heating to minimize adsorption and to reduce level of trapped impurities
- d. wash carefully to avoid peptizing precipitate

- e. if practical, redissolve and reprecipitate sample
2. Ion exchange - use either cation or anion exchange resins

Equilibrium equations:



R = Dowex 50, strong acid cation exchanger



R = Dowex 1, strong base anion exchanger

- a. Effects of crosslinkage:

Crosslinkage - amount of divinylbenzene incorporated into the polystyrene matrix.

Increased cross linkage results in:

1. smaller changes in bed volume for different ionic forms and ionic strengths
2. increase in selectivity when latter is dependent on relative ionic radii
3. increase in capacity per unit volume of wet resin

4. slower kinetics of ion exchange due to decreased rates of ionic diffusion in resin

b. Effects of resin particle size

A smaller particle size results in:

1. faster attainment of equilibrium
2. increased efficiency of separation for a given volume of resin
3. a decreased flow rate for the same pressure

c. Advantages of ion exchange technique:

- i. Multi-step separation
- ii. Used for carrier free separations
- iii. Can be rapid and very selective

Disadvantages:

- i. Some experience in handling often necessary for useful results.

d. Cation Exchange

Factors effecting affinities of different cations for strong acid cation exchange resin:

- i. In dilute solutions, the affinity increases with increasing crystal radius of cation,
 $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$

e. Anion exchange

Order of selectivity:

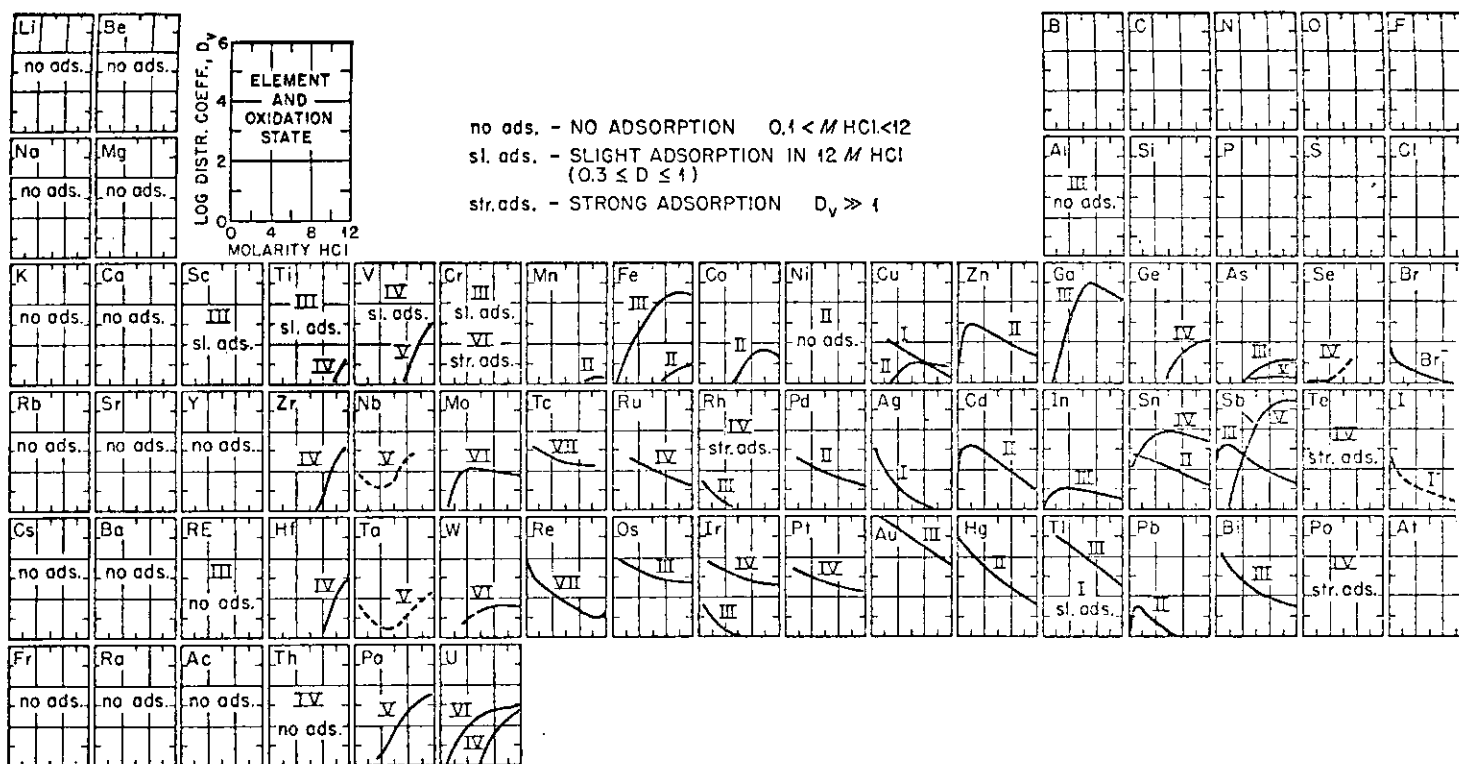
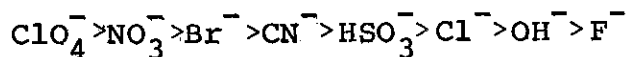


FIG. 2. Adsorption of the elements from hydrochloric acid by Dowex 1. Kraus and Nelson, Paper 837, Geneva Conf. Vol. 7 (1956).

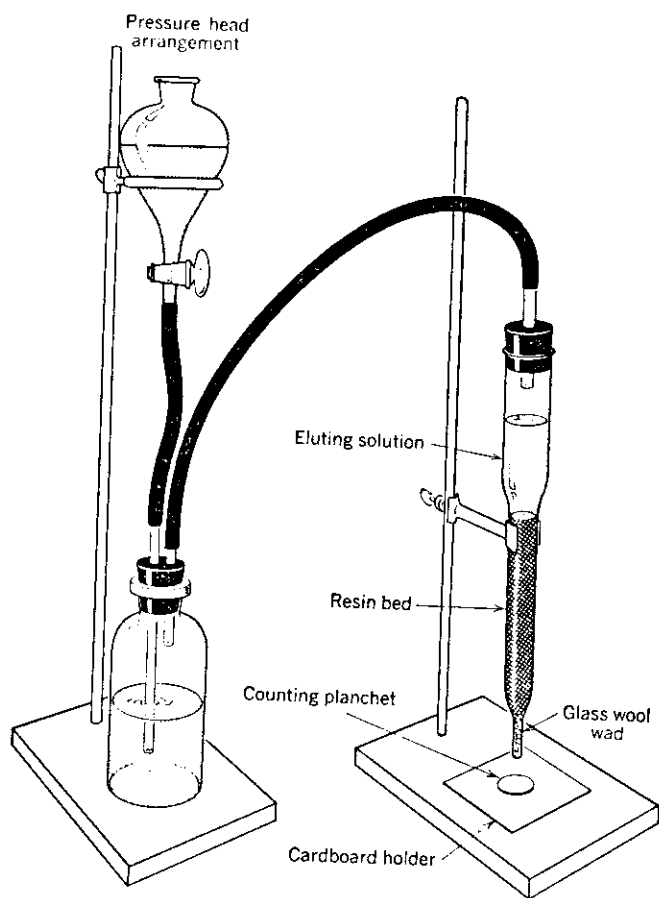


FIG. 3. Ion exchange elution column and pressure head.

3. Solvent Extraction - very similar to ion exchange.

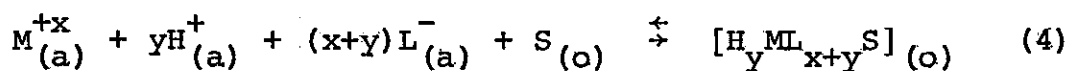
The desired metal ion is distributed between two immiscible liquid phases, usually water and

an organic solvent. The organic solvent may itself act as an extracting agent or the organic phase may consist of an extracting agent dissolved in an organic solvent.

a. Some typical solvent extraction systems

Cationic type:

- i. Extraction by an unionized organic solvent containing oxygen donor atoms - no diluent



Where M^{+x} - metal ion of charge x

H^{+} - hydrogen ion

L^{-} - monobasic ligand such as NO_3^{-}

S - organic solvent molecule acting as extractant

(a) - aqueous phase

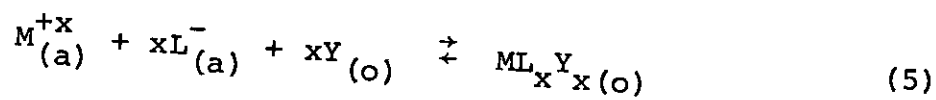
(o) - organic phase

Examples of S: diethyl ether

methy isobutyl ketone (MIBK)

isopropyl alcohol

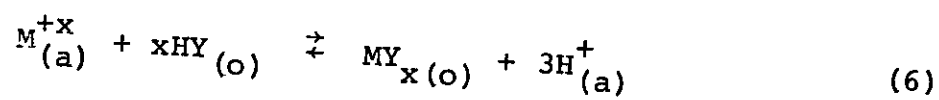
ii. Neutral phosphorous-based extractant dissolved in hydrocarbon diluent



Y - extracting agent

Ex: tributyl phosphate (TBP)

iii. Acidic extractants with oxygen donors dissolved in hydrocarbon diluent; usually extract through chelate formation



HY - acidic extractant

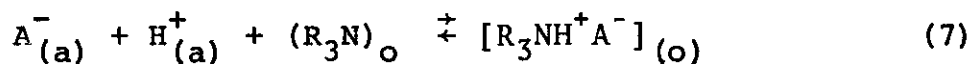
Ex: thenoyltrifluoroacetone (TTA)

di(2-ethylhexyl)phosphoric acid (HDEHP)

b. Anionic type:

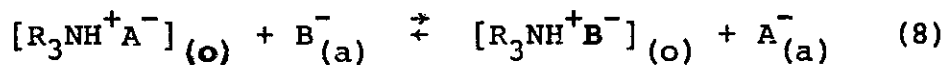
Amine extractants dissolved in a hydrocarbon diluent. Can be primary, secondary, or tertiary, amine or quaternary ammonium salts; Usually a high molecular weight amine.

Eqn. for tertiary amine (R_3N):

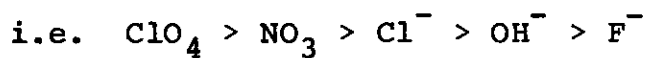


A^- = anion of an acid such as NO_3^- or a metal complex such as $FeCl_4^-$

$R_3NH^+A^-$ can undergo ion exchange:



Order of selectivity similar to that of anion exchange resins:



Advantages of solvent extraction:

- a. High selectivity
- b. Useful for carrier free separations
- c. Rapid, often faster than ion exchange
- d. Technique easier than ion exchange
- e. Wide variety of solvent extraction systems

Disadvantages:

- a. Single step separation

4. Chromatography

- a. Paper Chromatography - partition between a stationary aqueous phase supported by hydrophilic paper and a mobile organic phase.
- b. Electromigration - separation due to different velocities of ion under an electric field gradient. Both the solid and liquid phases are stationary with the liquid phase acting as a medium through which the ions migrates.
- c. Reversed-phase Chromatography - Solid support holds the organic phase as the stationary phase while the aqueous phase is mobile. Commonly

used as a column chromatographic technique in place of conventional ion exchange resins.

Ex: Extracting agent such a HDEHP absorbed on small glass beads (200-400 mesh), made into a column and separation on column by acidic eluant as in cation resin elution.

5. Distillation and Volatilization

- a. Distillation - similar to conventional method even at carrier free level.

TeCl_4 , SbH_3 , OsO_4 , I_2 are some compounds which can be distilled

Volatilization - when carrier free tracer is placed on surface and the temperature is raised, volatilization may begin below boiling point. Over narrow temperature range 90% or more of radioactive atoms are evolved from the surface.

C. Sample Preparation

1. Solution evaporation: good for small volumes of dilute or carrier free solutions. Solution spreads uniformly over counting planchet and solvent is evaporated under infrared lamp taking care to prevent splattering and consequent contamination of surrounding work area.

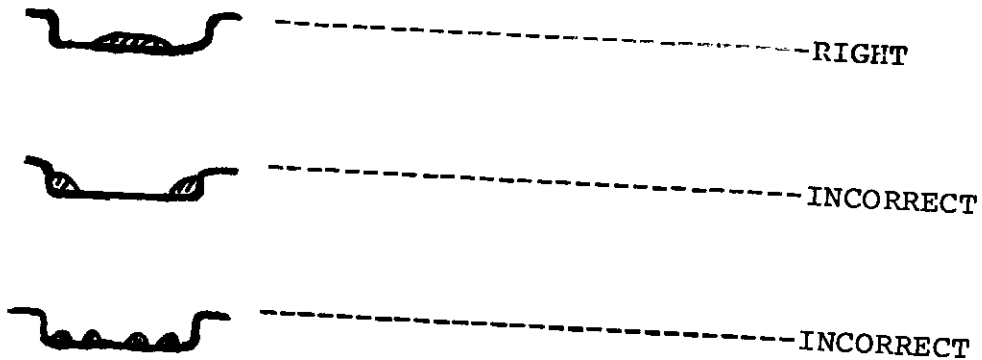


FIG. 4. Sample preparation by evaporation

2. If we have precipitation of carrier and radioactivity, the precipitate can be affixed to a counting pad by filtration. Pad then transferred to counting planchet.

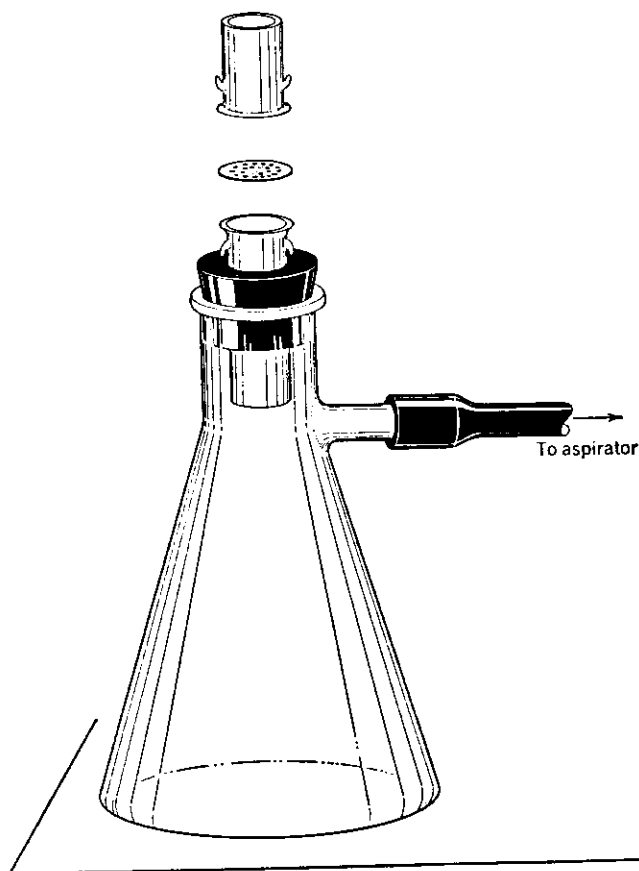


FIG. 5. Filter assembly for obtaining uniform deposits.

3. Electrodeposition: the desired cation is either deposited in metallic state or precipitated in an insoluble form on the electrode (usually a thin foil).

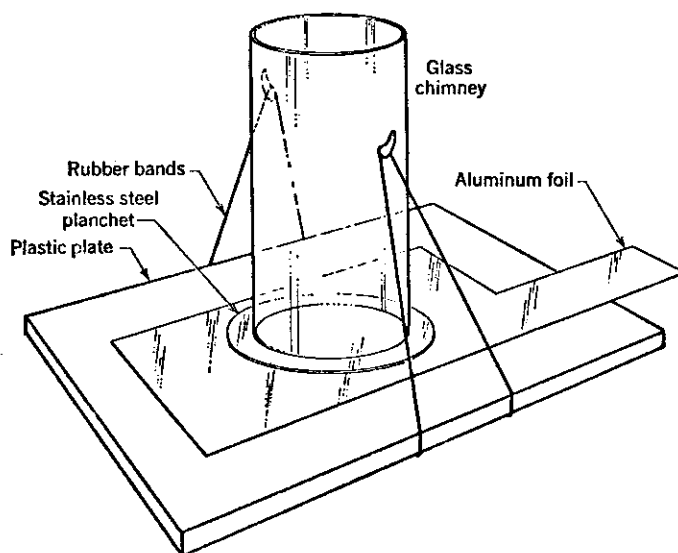


FIG. 6. Experimental arrangement for electrodeposition

4. Sublimation: elements or compounds are sublimed at high temperatures in a vacuum from a filament onto a counting planchet.
5. Liquid Samples: may be counted directly by liquid scintillation technique. Can also count gamma ray emitting radionuclides in a liquid sample using a NaI(Tl) well counter.
6. Gaseous Samples: usually avoided due to difficulties in handling.

SECTION II

Counting Efficiency

The following considerations are mainly for β emitting samples although in principle apply also to α and γ emitters.

A. Detector Efficiency = C

$$C = \frac{R \text{ (cpm)}}{R \text{ (dpm)}} = \frac{\text{measured count rate}}{\text{absolute disintegration rate}} \quad (9)$$

Also

$$C = f_e \cdot f_\gamma \cdot f_g \cdot f_b \cdot f_s \cdot f_a$$

1. f_e : counting efficiency of tube; $f_e = 1$ for good GM tube

2. f_γ : resolving time correction

Determine the resolving time τ for your particular counter system

Correction:

$$R_t = \frac{R_o}{1 - R_o \tau} \quad (10)$$

R_t = true cnt rate (cps)

R_o = observed cnt rate (cps)

τ = resolving time (sec)

3. f_g : geometry factor

4. f_b : back scattering factor; increases with increasing thickness of sample up to saturation or increases with z of sample backing material

5. f_s : self absorption factor

$$f_s = \frac{1}{\mu s} (1 - e^{-\mu s}) \quad (11)$$

s = sample thickness (mg/cm^2)

μ = absorption coefficient

$$\mu = \frac{22}{E^{1.33}} \text{ (cm}^2/\text{mg)}$$

E = energy of beta particle

6. f_a : absorption factor, includes absorption and scattering by sample covering, by air between sample and window, and by window.

NOTE: Counters are commonly calibrated by the use of SRM's (standard reference material) available from the National Bureau of Standards and from commercial suppliers. Rarely are the individual factors of Section II determined. Using the same planchets, sample position and counter all factors are invariant except the resolving time correction (a function of activity level) and the self absorption correction (a function of sample thickness).

SECTION III

Problems

1. Suggest one way of separating radioactive iodine from radioactive phosphate? [Hint: What would be the effect of the addition of AgNO_3 to a solution containing these two anions?]
2. A solution containing $^{210}\text{PbSO}_4$ ($t_{1/2} = 22$ yrs) was found to have a disintegration rate of 10,000 dpm per ml.
 - a. Can you precipitate the radioactive lead by the addition of 10 M SO_4^{-2} given the following information?
$$K_{sp} = [\text{Pb}^{+2}][\text{SO}_4^{-2}] = 1.1 \times 10^{-8}$$
 - b. How much inactive Pb carrier would be necessary to precipitate 99% of the ^{210}Pb in a 10M sulfate solution?
3. Twenty milliliters of a solution (solvent 1) containing 10^{-2} grams of iodine containing 25,000 dpm of I ($t_{1/2} = 8.07\text{d}$) is equilibrated with 10 ml of an immiscible solvent (solvent 2). Using the distribution coefficient K,

$$K = \frac{\text{conc. of solute in solvent 1}}{\text{conc. of solute in solvent 2}} = 20$$

calculate the weight of iodine in each solvent at equilibrium,

4. Using the results of problem 3, calculate the count rate in cpm of ^{131}I in each solvent assuming the efficiency of your counter is 7%.
5. What is the requirement for the purification of two substances by distillation whether they are radioactive or not?
6. Suggest a method for the separation of the following nuclides $^{40}\text{K}^+$, $^{232}\text{Th}^{+4}$, $^{140}\text{La}^{+3}$ and $^{131}\text{Ba}^{+2}$.
7. Two electrodes are placed in an aqueous solution of the radioactive metal chlorides of Zn, Fe, and Sn. The voltage which must be applied across the electrodes to cause deposition is

$$E_{\text{applied}} = E_{\text{cathode}} - E_{\text{anode}} + W$$

where W is the overvoltage. Given the following information, what are the possible cathode reactions? What is the anode reaction? Assuming $W = 0.2\text{V}$, at what applied voltages will these three metals be deposited?

	[E°(V)]
$1/2 \text{ Zn} \rightarrow 1/2 \text{ Zn}^{+2} + \text{e}^{-}$	0.76
$1/2 \text{ Fe} \rightarrow 1/2 \text{ Fe}^{+2} + \text{e}^{-}$	0.44
$1/2 \text{ Sn} \rightarrow 1/2 \text{ Sn}^{+2} + \text{e}^{-}$	0.14
$1/2 \text{ H}_2\text{O} \rightarrow 1/4 \text{ O}_2 + \text{H}^{+} + \text{e}^{-}$	-1.23
$\text{Cl}^{-} \rightarrow 1/2 \text{ Cl}_2 + \text{e}^{-}$	-1.36