

## CHAPTER II

### THEORY

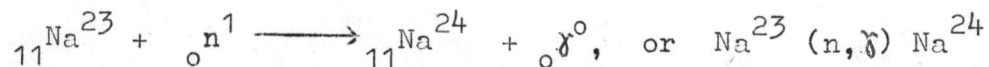
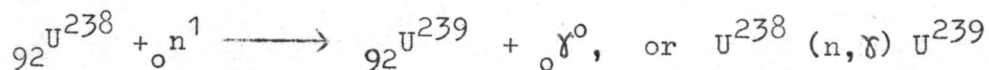


#### 2.1 Neutron Activation Analysis

##### 2.1.1 Basic Concepts of Neutron Activation Analysis (NAA)

Activation analysis is commonly considered a method of analysis for chemical elements in trace quantities. A radioactive nuclide is formed when an element is bombarded by neutrons or charged particles such as electrons and protons etc.

A reaction used extensively in activation analysis is the (n,r)-reaction, which is shown as examples in the following equations :



In a nuclear reactor, stationary conditions are established when the number of neutrons released in a given volume is about equal to the number of neutrons which participate in new fission acts. Neutrons from a nuclear reactor are composed of thermal and fast neutrons. Thermal neutrons are neutrons with an energy of about 0.025 eV.

The interactions between thermal neutrons and most of the nuclides through the (n,r) reaction produce radioisotopes which can be identified by their characteristic decay rates and energies of the emitted radiations. The amount of radioisotope produced can be calculated from the well-known activation equation :

$$A = N\sigma\phi(1 - e^{-\lambda t}) \quad (2.1)$$

where :

A = induced activity at the end of irradiation (dps)

N = number of target atom present

$\sigma$  = cross section of an element ( $\text{cm}^2/\text{atom}$  or barn)

$\phi$  = thermal neutron flux ( $\text{n}/\text{cm}^2/\text{s}$ )

t = irradiation time

$\lambda$  = decay constant of product nuclide

$$= \frac{0.693}{t_{1/2}}$$

$t_{1/2}$  = half-life of product nuclide.

Half-life ( $t_{1/2}$ ) and irradiation time (t) must be the same unit of time.

Since

$$N = \frac{\text{No.W.f}}{M} \quad (2.2)$$

where :

No = Avogadro's number ( $\text{atom}/\text{mol}$ )

$W$  = weight of element (g.)

$f$  = fractional isotopic abundance of the target nuclide

$M$  = atomic mass of the element;

substituting  $N$  into equation (1), the following equation is obtained :

$$A = \frac{No. \cdot W \cdot f \cdot \phi \cdot \sigma}{M} (1 - e^{-\lambda t}) \quad (2.3)$$

or

$$W = \frac{M}{No. \cdot f \cdot \phi \cdot \sigma (1 - e^{-\lambda t})} \quad (2.4)$$

Theoretically it is possible to calculate the amount of element present in a sample from equation (2.4). However in practice, the absolute activity cannot be determined easily since the value of neutron flux ( $\phi$ ) and the reaction cross section of an element ( $\sigma$ ) are not exactly known. Therefore, by comparing the count rate of a standard with that of the sample, one can determine the amount of each element in the sample by the following equation :

$$\frac{\text{weight of element in sample}}{\text{weight of element in standard}} = \frac{\text{count rate of sample}}{\text{count rate of standard}}$$

### 2.1.2 Sensitivity of the Method of NAA

If the irradiation time is long compared to the half-life of the radioisotope, the term  $(1 - e^{-\lambda t})$  in equation (2.4), known as the saturation factor, approaches 1. From the

equation of neutron activation i.e. equation (2.3) or (2.4), it is obvious that the sensitivity of NAA will be greater the higher the efficiency of the detection system, the higher the neutron flux, the greater its activation cross-section and isotopic abundance.

### 2.1.3 Errors in the Method of Neutron Activation

#### Analysis

The technique of neutron activation analysis has its own special advantages, so it has its own particular set of errors. Fortunately, these errors are comparatively few and can, in general, be minimized if not eliminated.

#### 2.1.3.1 Errors Due to Irradiation

The main source of error is due to the fact that standard and sample are not exposed to the same neutron flux; or in other words, if there is a flux variation as a function of irradiated position. Neutron flux variation is possible as a function of time and irradiation position.

For this reason, standards and samples are irradiated together in one container. It is necessary to make sure that the samples and standards are placed as close together as possible.

#### 2.1.3.2 Errors Due to Interfering Nuclear Reaction

The interference will obviously be more or less serious, depending on the relative concentrations of the target nuclides

in the samples, on the ratio of fast to thermal neutron flux and on the ratio of the cross sections of various nuclear reactions. Fortunately, the cross sections for (n,p) and (n, $\alpha$ ) reactions are generally quite low compared to the (n, $\gamma$ ) cross sections, so that this interference will be less important or even negligible if the irradiation is carried out in a well thermalized neutron region, such as the thermal column.

#### 2.1.3.3 Errors Due to Radiation Measurement

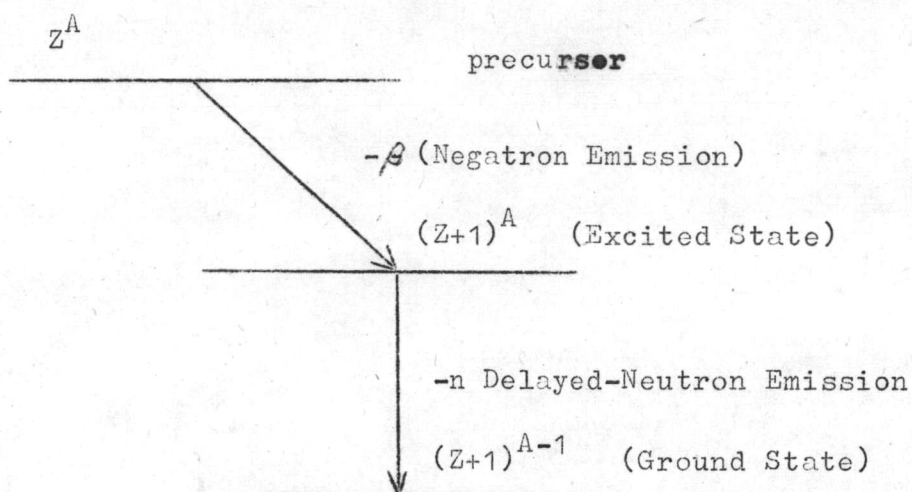
In the comparative technique, the counting geometry for standards and samples should be the same. If possible, activities of the standards and samples should be of the same order of magnitude.

#### 2.1.4 Quantitative Analysis of Uranium by NAA

The analysis of uranium by the technique of neutron activation can be performed in 2 different ways, i.e. the delayed neutron counting technique and the gamma spectroscopic technique.

The  $\beta$ -decay of a fission product produces, in many cases, excited states of the daughter nucleus. In a few cases, the excitation energy exceeds the binding energy of a neutron. As a result of this process, neutrons are emitted at a measurable time after the fission act. The decay scheme can be shown as follows :





By measuring the delayed neutron emission after fission with  $\text{BF}_3$  detectors, the uranium content can be analysed.

The irradiation of uranium with neutrons produces, besides the fission reaction, also the  $(n, \gamma)$ -reaction. U-239 produced from the reaction is  $\beta$ -unstable and decays to Np-239 with a half-life of 23.5 minutes. Np-239 decays successively to Pu-239 with a half-life of 2.35 d. The decay schemes of U-239 and Np-239 are given in Figure 2.1 and Figure 2.2 respectively. The decay scheme of Np-239 is so complicated that only semiconductor detectors could resolve all the energies. So, the gamma-spectroscopic method for the determination of uranium could be commenced either by measuring the gamma spectrum of U-239 or that of Np-239. As the half-life of U-239 is short, the measurement must be performed soon after irradiation whereas a decay time of several days is required for the measurement of Np-239. The large excess of matrix elements necessitates the use of chemical processing

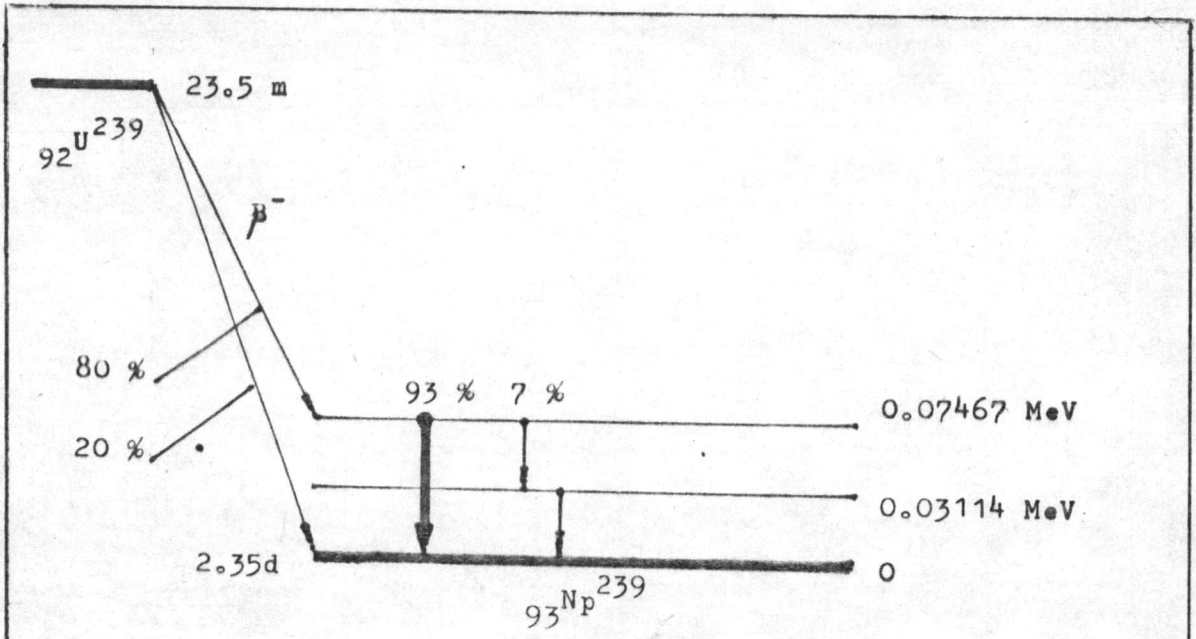


Figure 2.1 The decay scheme of U<sup>239</sup>

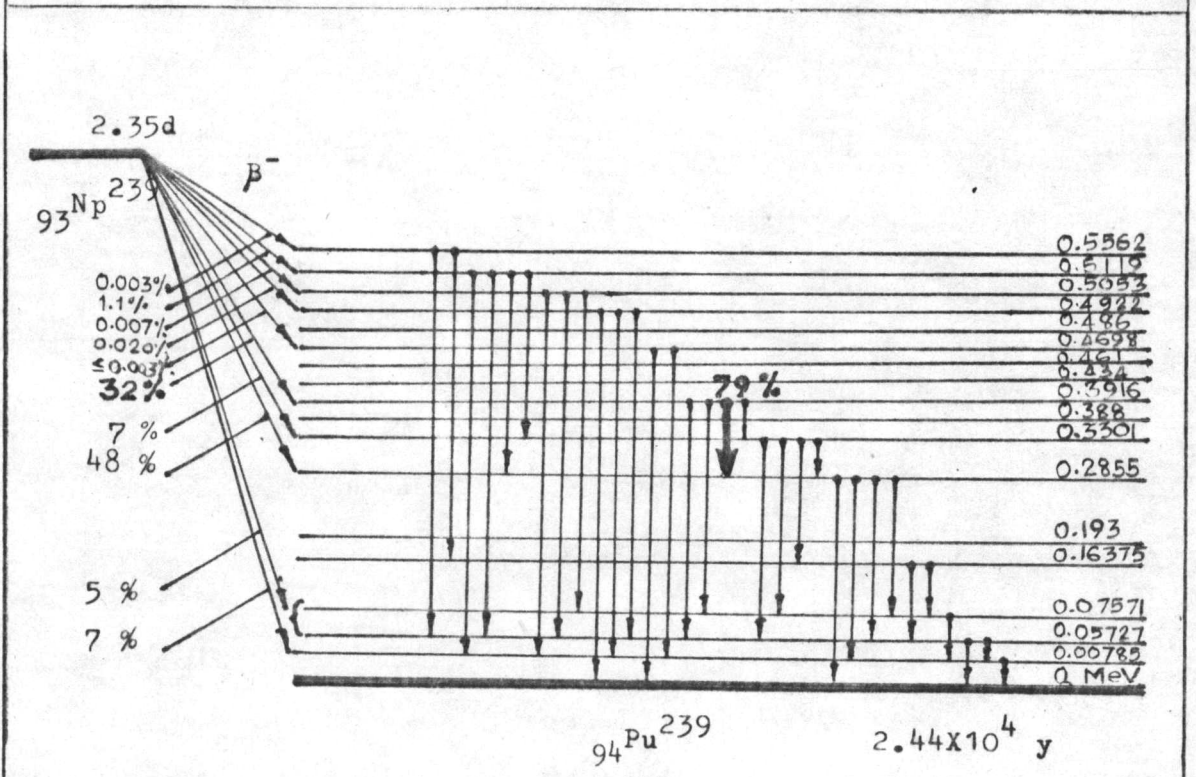


Figure 2.2 The decay scheme of Np<sup>239</sup>

prior to radiation measurement. As the resonance integrals of uranium is high (see Table 2.1), it is possible to reduce the matrix activities by irradiating the samples in a reactor with resonance and fast neutrons behind a cadmium shield.

Compared with an irradiation with the whole reactor neutron spectrum, the matrix activities are reduced to 1 % while those of uranium ( $\text{Np}^{239}$ ) to about only 50 %.<sup>(23)</sup> This relative diminution

Nuclide	Thermal cross-section, barn	Resonance cross-section, barn
$^{238}\text{U}$	2.7	280

Table 2.1 Neutron capture cross-section of uranium with thermal and resonance neutron<sup>(23)</sup>

of matrix activities allows the r-measurement of  $^{239}\text{Np}$  as early as after two days cooling time. For quantitative analysis, the 74.5 keV of U-239 and the 106 keV of Np-239 are generally used. As the measurement of U-239 is more rapid, this method is used in the present investigation.

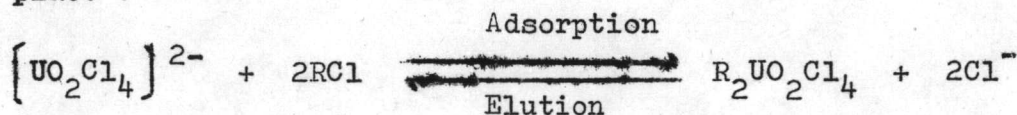
#### 2.1.5 Separation of Uranium through Anion Exchange Resin

In chloride media, uranium forms complexes as  $\text{UO}_2\text{Cl}_2$ ,



~~$\left[ \frac{1}{3} \text{H}_2\text{O} \left( \frac{2}{3} \text{H}_2\text{O} \right)_3 \left( \text{UO}_2\text{Cl}_4 \right)_2 \right]^{3-}$  and  $\text{UO}_2\text{Cl}_4^{2-}$ .~~ In alcoholic solution the complex  $\text{UO}_2\text{Cl}_4^{2-}$  is predominant whereas the form  $\text{UCl}_6^{2-}$  is also present.

When the solution of uranium is passed through a bed of anion exchange resin, a reaction of the following type takes place :



when :

R = A quaternary ammonium salt which structure is shown in Figure 2.3

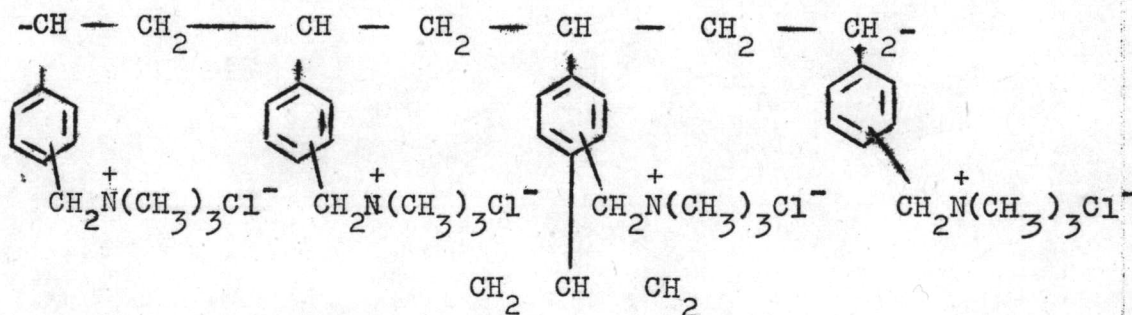


Figure 2.3 Structure of a quaternary ammonium anion exchange resin.

Resin of the similar structure from different producers which could be used are summarized in Table 2.2

Table 2.2 Strong Base Anion Exchange Resin from different Producers

Type	Functional Group	Trade Name	Approximate sp. Capacity (meq/cm <sup>3</sup> )	Maximum Temp. (°C)	Degree of cross linking (%)	pH Limits	Producers
strong base	crosslinked polystyrene -NR <sub>3</sub> <sup>+</sup>	Amberlite IRA-400	1.40	60	8	1-12	Rohm & Haas Co.
		Amberlite IRA-401	1.00	60	4	1-12	Rohm & Haas Co.
		Amberlite IRA-402	1.20	60	6	1-12	Rohm & Haas Co.
		Amberlite IRA-410	1.40	40	8	1-14	Rohm & Haas Co.
		Dowex 1 x 8	1.33	50	8	1-14	Dow Chemical Co.
		Zerolit FF (ip)	1.20	60	-	1-14	Am. Zeolite Corp.
		Duolit A 101 D	1.20	60	-	1-14	Chemical Process Co.

## 2.2 Fluorometry

### 2.2.1 Basic Concepts of Fluorometry

Most substances that absorb ultra-violet or visible light dissipate the excess energy in the form of heat or through collisions with neighboring atoms and molecules. However, a number of important substances lose only part of this excess energy as heat and emit the remaining energy as electromagnetic radiation of longer wavelength. This process of radiation emission is collectively termed luminescence, further classified as either fluorescence or phosphorescence.

In general, the absorption process raises a molecule from the ground electronic and vibrational state to an excited electronic and vibrational state. When a molecule has an excited electronic state that is more stable than usual, the excess vibrational energy will be dissipated by collisions while the molecule remains in the excited electronic state, later the molecule will either return directly to the ground electronic state by emission of radiation (fluorescence) or, less commonly, it may shift to a metastable triple level before emitting radiation (phosphorescence). A typical lifetime for an excited electronic state is about  $10^{-8}$  s, and materials exhibiting fluorescence generally reemit excess radiation within  $10^{-8}$  to  $10^{-4}$  s of absorption. The lifetime of phosphorescence is much longer than fluorescence, generally ranging from about  $10^{-4}$  to 20 s or longer.



The schematic energy-level diagram is shown in Figure 2.4 and 2.5

Uranium emits fluorescent radiation when it is fused with a flux mixture containing  $\text{NaF}$ ,  $\text{Na}_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$  at a temperature about  $650^\circ$  celsius. At low concentration, the intensity of the fluorescent radiation,  $I_f$ , will be directly proportional to the concentration  $C$  of the absorbing species.

If Beer's law holds, the fraction of transmitted light  $T$  is given by

$$T = \frac{P}{P_0} = e^{-abC} \quad (2.2.1)$$

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where  $P_0$  = incident radiant power  
 $P$  = transmitted radiant power  
 $a$  = absorptivity  
 $b$  = length of cell path  
 $C$  = concentration of absorbing substances.

The corresponding fraction of light absorbed is then :

$$1 - \frac{P}{P_0} = 1 - e^{-abC} \quad (2.2.2)$$

When Eq. (2.2.2) is rearranged, the amount of light absorbed is :

$$P_0 - P = P_0 (1 - e^{-abC}) \quad (2.2.3)$$

where

$$1 - e^{-abC} = 2.3abC - \frac{(2.3abC)^2}{2!} + \frac{(2.3abC)^3}{3!} \dots (2.2.4)$$



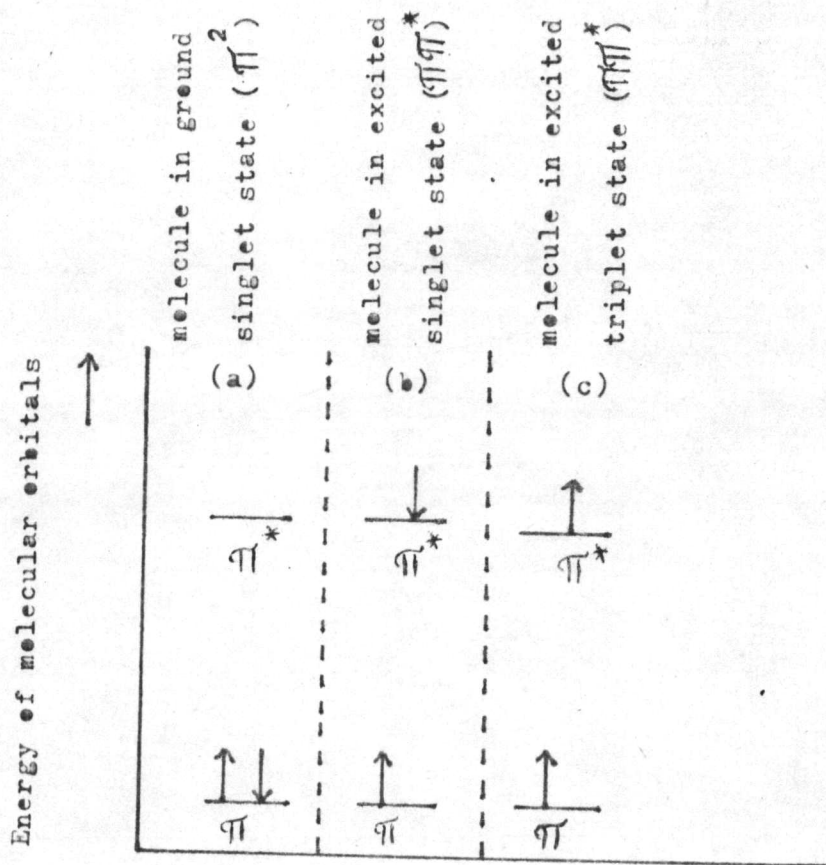


Figure 2.4 Examples of molecules with electrons in various spin configuration

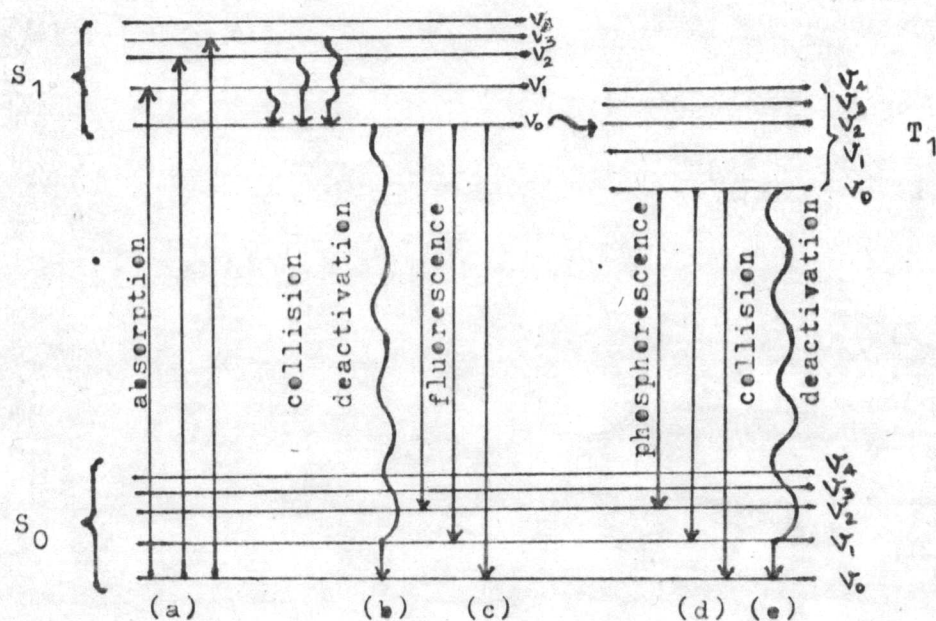


Figure 2.5 Schematic energy-level diagram illustrating the energy changes involved in absorption, fluorescence, and phosphorescence. (Straight arrows represent radiation photons; wavy arrows represent radiationless collisional deactivation,  $v$  = vibrational levels,  $S_0$  = singlet ground state,  $S_1$  = singlet first excited state,  $T_1$  = triplet first excited state )

The intensity of the fluorescent radiation,  $I_f$ , is related to the amount of light absorbed according to the following equation :

$$I_f = k\phi_f (P_o - P) \quad (2.2.5)$$

where

$k$  = proportionality constant that depends on the instrument (the efficiency of the detector system and the geometry)

$\phi_f$  = the quantum efficiency of fluorescence (the ratio of quantum emitted to the quantum absorbed in a unit of time)

At low concentration,

$$I_f = k\phi_f (2.3abC) \quad (2.2.6)$$

Experimentally, the uranium content of the fused-flux can be calculated according to the following relation :

Microgram of U in Unknown = microgram of U in **Standard**

$$X \frac{\text{average unknown reading} - \text{blank}}{\text{average standard reading} - \text{blank}}$$

### 2.2.2 Quantitative Analysis of Uranium by the Fused Pellet Method

A trace of uranium fused in the fluorometric flux mixture gives a very intense yellow-green fluorescence spectra with most intense band at  $5546^{\circ}\text{A}$  when subjected to excitation by ultraviolet light at  $3650^{\circ}\text{A}$ . High sensitivity and precision



are obtained for the determination of uranium between 0.1 ng and 10  $\mu$ g.

Many chemical compounds and mixtures have been used as flux in the fluorometric determination of uranium. Flux selection is complicated by many properties required of an acceptable flux. Flux mixtures currently in use may be placed in the following two categories :

High-Carbonate Fluxes Low-melting ( $\sim 600^{\circ}\text{C}$ ) materials which after fusion and solidification are readily removed from the dish in a single button. These fluxes are exemplified by sodium fluoride-sodium carbonate-potassium carbonate mixtures containing 1 to 10 % of sodium fluoride.

High-Fluoride Fluxes High-melting ( $\sim 1000^{\circ}\text{C}$ ) materials which after fusion and solidification cannot be removed from the dish without fracturing the button. Fluxes of this type are exemplified by pure sodium fluoride or a 2 % lithium fluoride -98 % sodium fluoride mixture.

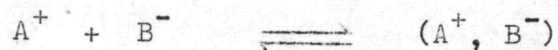
The combination of excitation at  $3650^{\circ}\text{A}$  and fluorescence at  $5546^{\circ}\text{A}$  makes this system almost specific for uranium. However, it must not be forgotten that many elements produce quenching effects, and therefore a preliminary separation of uranium from other elements is essential.



### 2.2.3 Solvent Extraction of Uranium

#### 2.2.3.1 Ion Association Complex

In addition to coordination compounds, there are a large number of uncharged compounds formed by the association of oppositely charged ions in pairs or clusters of higher order. Extractable species are chelates existing in the organic solvent as ion association aggregates. Two ions  $A^+$  and  $B^-$  associate to form  $(A^+, B^-)$  according to the equation



The formation of an extractable species depends on the combined action of anions such as halides, thiocyanate or nitrate, and oxygen-containing organic compounds such as alcohols, ethers, ketones and esters in displacing the coordinated water from the metal. When the oxygen atom of the solvent molecule coordinates with the metal ion the term "oxonium" extraction system is applied.

#### 2.2.3.2 Salting-Out Agents

Salting-out agent is applied to those electrolytes whose presence greatly enhances the extractability of complexes particularly those encountered in oxonium extractions, for example, the complete removal of uranium from a uranyl nitrate solution by ether extraction. Mundy, Hecht and Grunwald<sup>(23)</sup> independently discovered that the addition of ammonium nitrate to the aqueous phase greatly enhanced the uranium extraction.

The important action of the salting-out agent is to build up water molecules around itself as oriented dipoles. The water molecules thus become unavailable as "free solvent"

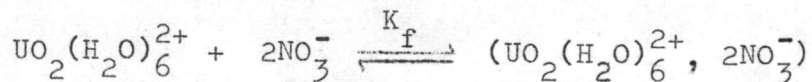
The addition of inorganic salt to the aqueous phase increases the distribution ratio of the metal complex in favor of the extracting phase.

### 2.2.3.3 Extraction of Uranyl Nitrate

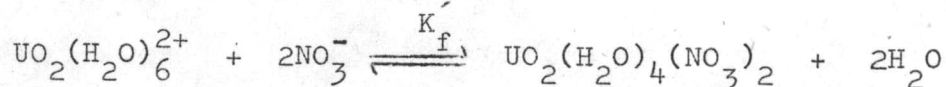
Solvent extraction has long been applied by many investigators in separating uranium from numerous elements in nitrate solution. In some solvents, such as ethers and esters, uranyl nitrate exists as a coordination compound. In the more strong basic solvents, notably the alcohols and water, the solvent occupies all the coordination positions and consequently the species extracted is an ion association complex.

The reactions involved in the distribution of uranyl nitrate between an oxonium solvent and water may be described as follows:

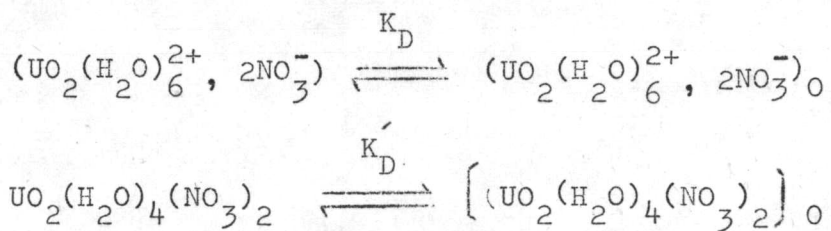
1) Formation of complex



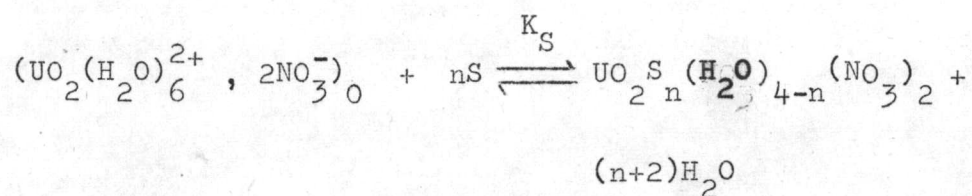
or, if the water activity is low



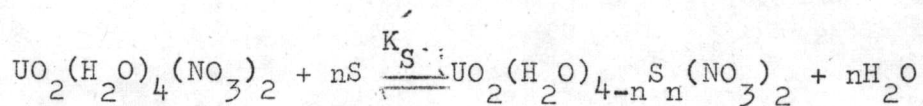
2) Distribution of the complex



3) Reactions in the organic phase



or



If S represents a strong basic solvent such as butanol, then the following reaction will take place

