CHAPTER II

THEORETICAL BACKGROUNP

2.1 Neutron Activation Analysis (1), (2), (3), (4)

2.1.1 Basic Concept of Activation Analysis. Activation analysis is commonly considered a method of analysis for chemical elements in trace quantities. It is based upon the principle that radioactive isotopes can be formed in an interaction of an element with a nuclear particle such as neutron, electron and proton etc. By measuring the induced radioactivity, the element and its concentration in the sample material can be determined.

2.1.2 Neutron Activation. Neutrons from a nuclear reactor is composed of thermal and fast neutrons. Thermal neutrons are neutrons with energy of about 0.025 eV, which after attacking a target induce principally the (n, ɤ)reaction The induced radioactive nuclides are indentified by their characteristic decay rates and energies of emitted radiations. The amount of radioactivity produced can be calculated from the equation:

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

where

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

N = number of target atom present

σ = crossection of an element (cm^2/atom or barn)

$\emptyset$ = thermal neutron flux (n/cm^2 s)

t = irradiation time

λ = decay constant of product nuclide = $0.693/t_{1/2}$

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

since

$$N = \frac{N_o \, W \, f}{At.Wt.} \qquad \cdots\cdots\cdots\cdots(2.2)$$

where

N_o = Avogadro's number (atom/mole)

W = weight of element (g)

f = fractional isotopic abundance of the target nuclide

At.Wt. = atomic weight of the element

we obtained, by substituting N in equation (2.1) :

$$A = \frac{N_o \, W \, f \, \sigma \, \emptyset \, (1-e^{-\lambda t})}{At.Wt.} \qquad \cdots\cdots\cdots\cdots(2.3)$$

or

$$W = \frac{A \; At.Wt.}{N_o \, f \, \sigma \, \emptyset \, (1-e^{-\lambda t})} \qquad \cdots\cdots\cdots\cdots(2.4)$$

Theoretically, it is possible to calculate the quantity of various elements present in a sample from equation(2.4). In practice, however, the absolute activity cannot be determined easily since the exact value of $\emptyset$ and σ are not known. For this reason, the comparative method is generally used. That is, to compare the activity of the sample with a standard whose composition and concentration are exactly known. Thus, the quantity

of each element in a sample can be calculated by the equation:

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

2.1.3 Sensitivity of Neutron Activation Analysis. The sensitivity or the minimum amount of an element that can be detected is an important information in choosing an analytical technique. From the equation of neutron activation, i.e. equation (2.3) or (2.4), it is obvious that, the major parameters that affect the sensitivity for the determination of an element are its cross-section, maximum neutron flux available and the length of irradiation time.

2.1.4 Accuracy and Precision. Precision and accuracy are also important requirements for the quantitative analysis. Factors that affect accuracy and precision are as follow:

a. Technique of Irradiation. Error may be induced if the sample and the standard are not exposed to the same neutron flux, or in other words, if there is a flux variation as a function of irradiated position. For this reason standards and samples are placed close to each other and irradiated together in a container. Inaccurate results will also be obtained if neutron self-shielding occurs in the samples or in the comparators.

b. Interfering Nuclear Reactions. This interference will obviously be more or less serious, depending on the relative concentration of the target nuclides in the samples, on the ratio of fast to thermal neutron flux and on the ratio of σ of various

nuclear reactions. Fortunately, the σ of the interfering reactions are generally low compared to that of the (n, γ) reaction. This interference will be less important or even neligible if the irradiation is carried out in a well thermallized neutron spectrum.

c. Technique of Radiation Measurement. If non-destructive activation analysis is performed, suppression by higher energy γ-photopeak from interfering nuclides may cause errors in the result. Care must be taken that the counting geometry for standards and samples is similar. If possible, activity of the standard and the sample should be of the same order.

2.2 Chromatography. The term "Chromatography" has been defined primarily as a separation process which is used for the separation of essentially molecular mixtures(5). All chromatographic separation techniques depend on the distribution of the molecules of a mixture between two or more phases. The various types of chromatography include adsorption chromatography, fluid partition chromatography and ion-exchange chromatography. In fluid partition chromatography, the technique applied in the present study, distribution takes place between an essentially stable "liquid" phase sorbed to a support and a mobile fluid in intimate contact with it. Dithizone in CCl_4 and di(2-ethylhexyl) phosphoric acid in cyclohexane were used as stationary liquid phase.
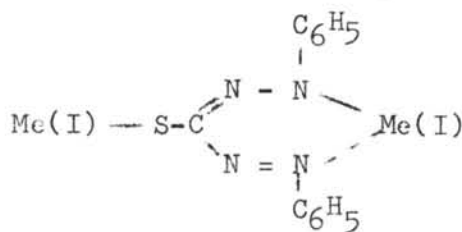
Dithizone or diphenyl thiocarbazone,

$$S = C \underset{\diagdown N \,=\, N\text{-}C_6H_5}{\overset{\diagup NH\text{-}NH\text{-}C_6H_5}{}}$$
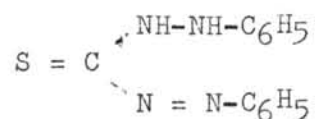
a well known chelating agent in solvent extraction, is a violet-black solid which dissolves in most organic solvents (6). CCl_4 and $CHCl_3$ are two solvents mostly used in the preparation of dithizone solution for analytical purpose. When a solution of dithizone in organic liquid is shaken with an aqueous solution of a reacting heavy metal, an internal complex dithizonate is formed which generally is soluble in the organic solvent. Two kinds of metal dithizonate can be found, the keto and the enol forms of the primary and the secondary dithizonates. Dithizonates of an univalent metal are given as an example :
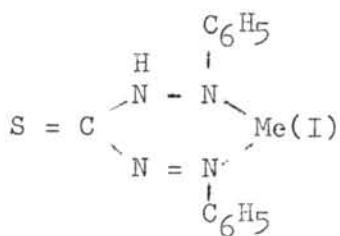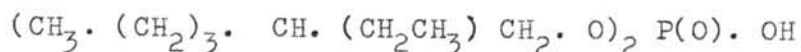
primary dithizonate   secondary dithizonate

Di (2-ethylhexyl)phosphoric acid,

$$(CH_3 \cdot (CH_2)_3 \cdot CH \cdot (CH_2CH_3) \, CH_2 \cdot O)_2 \, P(O) \cdot OH$$

another agent frequently used as complexing agent in liquid extraction for some metals (7). The metal, in forms of ion, will react with the agent to form an uncharged molecule that can be extracted into an organic phase. The action of such an extraction agent has frequently been called "liquid ion exchange".