CHAPTER 1

INTRODUCTION

1.1 Uranium

1.1.1 General (1, 2)

Uranium was discovered in 1789 in pitchblende ore $[UO_{2.2}\text{-}UO_{2.67}\ (U_3O_8)]$ by Martin Klaproth. It has an atomic number of 92 and relative atomic mass of 238.03. It is a member of the actinide series and consists primarily of three isotopes, namely U-234 (0.005%), U-235 (0.711%), and U-238 (99.283%). The radioactive properties of uranium were discovered in 1896 by Henri Becquerel. Natural uranium has a physical half-life of 4.5×10^9 years.

Uranium is ubiquitous in soils and rocks of the earth' s crust, with concentrations ranging from 1 to 4 mg/l. It is also found in seawater at concentrations of about 0.001 to 0.003 mg/l. In general, uranium is more abundant than mercury, silver, antimony or cadmium, and is similar in abundance to molybdenum and arsenic. The most important minerals of commercial uranium deposits are Uraninite $[UO_2]$, Pitchblende $[UO_{2.2}\text{-}UO_{2.67}\ (U_3O_8)]$, Carnotite $[K_2\ (UO_2)_2\ (VO_4)_2 \cdot nH_2O]$ and Autunite $[Ca\ (UO_2)_2\ (PO_4)_2 \cdot nH_2O]$.

Uranium metal is highly reactive and also forms numerous intermetallic compounds (Fig 1.1.1)

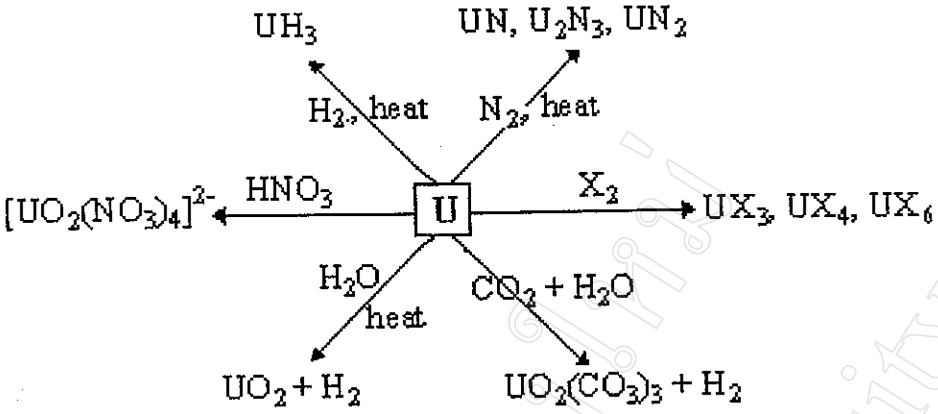

Fig. 1.1.1 Some reactions of uranium [X = halogen]

In aqueous solution, uranium may exist in the form of simple ions such as U^{3+} which is unstable ion, U^{4+}, UO_2^{+} and UO_2^{2+} (uranyl ion). Uranium ions are hydrolysed in solution, the degree of hydrolysis decreasing in the order $U^{4+} > UO_2^{2+} > U^{3+}$.

1.1.2 Applications of uranium (3, 4)

Uranium is used as the principal fuel for nuclear power reactors. Uranium oxide fuels (U_3O_8) are enriched in U-235 to increase the ability of the fuel to sustain a nuclear chain reactor. U-238 serves as a raw material for production of the nuclear fuel Pu-239. The fission of one atom of U-235 releases approximately 200 MeV of thermal energy. The heat is used to produce steam for driving turbine generators, which then generate electricity. One pound of uranium oxide fuel releases thermal energy equivalent to that from 2,063,880 litres of oil or 8 tons of lignite. Nuclear reactors can provide power for ships and submarines.

Uranium is also used in small research and isotope production reactors and has military applications : U-235 is used as the fissionable component of nuclear weapons

: U-238 is used in armor-piercing shells, ship or aircraft ballast, and counterbalances. Uranium also provides various applications in the chemical industry and is used for making coloured ceramic glazes.

Uranium is toxic in the same manner as other heavy metals such as lead, copper, arsenic and antimony. It is chemically toxic to kidney, liver and muscle tissues. It is also a radiation hazard due to the particles produced in its decay.

1.1.3 Determination of uranium

The determination of low uranium levels in nature is very important in prospecting works and for environmental protection. Numerous methods have been developed for various types of sample. Uranium dioxide has been dissolved and preconcentrated onto a column of tributylphosphate–levextrel resin prior to determination by inductively coupled plasma atomic emission spectrometry [ICP-AES] with a detection limit of 0.02 to 1.6 μg/g of sample (5). Solvent extraction with ICP-AES has been applied to the determination of uranium in mineral samples, solvent extraction being used to separate uranium from interfering elements. A linear range was found from 0.5 to 50 mg/l of U and the detection limit was 0.02 mg/l (6).

Inductively coupled plasma mass spectrometry [ICP-MS] has been reported as a highly sensitive techniques for analysing uranium in human plasma and urine at a detection limit of 2 ng/l (7). Sample pretreatment is needed for samples containing aluminium. Uranium was extracted into tributyl phosphate in cyclohexane and back-extracted into diluted hydrochloric acid, prior to being determined by ICP-MS, with a linear range of 0.05 to 50 ng of U at a detection limit of 7 pg/g of sample (8). Flow Injection Analysis [FIA] methods have been developed for the determination of uranium. FIA combined with ICP-MS has been used to improve sensitivity and selectivity for measurement of the short-lived radionuclide [U-234] in soil samples. The flow injection system was used to separate and concentrate radionuclides by solid-phase extraction. The limit of detection was 0.02 ng/g of sample (9).

Neutron activation analysis [NAA] techniques have been used to determine uranium in blood, urine and hair with detection limits of 1-2 pg/ml or /g (10). Traces of uranium can be determined by the induced radioactivity. Radiometric methods which detects alpha or gamma-rays from the decay products of uranium are available. Alpha-spectrometry can be used to analyse uranium in soil samples (11). Gamma-spectrometry was used to analyse natural uranium fuels (12).

High performance liquid chromatography [HPLC] with thermal lens detection has been used to determine uranium : the thermal lens effect being obtained by a dual laser arrangement focused on the flow cell. By using this technique uranium in sea water can be determined at a detection limit of 1 ng (13).

X-ray fluorescence [XRF] has been reported for the determination of uranium in surface and underground water. Uranium was pretreated by solvent extraction and precipitation. The detection limit was found to be 0.06 μg/l (14).

Spectrophotometric methods are the ones most commonly used for uranium determination. They can be applied to the analysis of a large variety of materials over a wide range of uranium concentrations. Most methods are based on the formation of chelate complexes. Several reagents such as 1-(2-pyridylazo)-2-napthol [PAN] (15), Arsenazo III (16), Chlorophosphonazo-mN (17) and ascorbic acid (18) have been reported to be highly sensitive but chemical separation steps are needed to improve selectivity. Uranium in water has been preconcentrated on a Dowex 50-X column by an FIA on-line technique prior to being determined by colour formation with Arsenazo III. The linear range was found to be 0.5 to 100 μg/l and the detection limit was 0.5 μg/l (19). An FIA in-valve preconcentration technique was also developed for separation and preconcentration of uranium in mineral samples before determination by means of complex formation with 1-(2-pyridylazo) resorcinol [PAR] with a detection limit of 0.27 μg of U and a linear range up to 7 μg of U (20).

Fluorimetric methods are very sensitve and quite specific for uranium determination. The technique is usually employed for samples that contain too little uranium to be analyzed spectrophotometrically. The determination can be based on fusion of the sample as a pellet with a sodium fluoride-sodium carbonate-potassium carbonate flux [$NaF-Na_2CO_3-K_2CO_3$]. The fluorescence is measured under ultraviolet light by reflection. The limitations of fusion techniques are the necessity for careful control of the fusion temperature and of the atmosphere during fusion, in order to obtain analytical reproducibility. Because the fused pellet is not easily removed from the dish, the fluorescence of each pellet must be measured in the dish, and the reflectivity of accordingly affects the amount of light reaching the radiation detector. It is necessary to clean and polish each dish after use by a tedious, carefully controlled, and detailed procedure. Fluorescence determination in solution is more convenient, but is often necessary to dilute the sample or to separate the uranium from the matrix so as to avoid quenching of the fluorescence by other elements in the sample. Liquid systems are also more convenient for preconcentration of the sample. Some fluorimetric methods for the determination of uranium are listed in Table 1.1 .

Table 1.1 Some fluorimetric methods for the determination of uranium

Sample	**Reagent & Conditions**	**Remarks**	**Ref.**
Sea water	Reagent = Fluran U in NaF/ammonia solution, pH 9.3, adsorbed on activated silica gel column. λex = 365 nm, λem = 493 nm	range 0.05-100 mg/l	21
Rock	Reagent = Rhodamine-B U separated by a flotation procedure with sodium dodecanoate in 95% ethanol λex = 555 nm, λem = 575 nm	range 0 - 0.5 μg	22
Water	Reagent = Rhodamine B + benzoic acid U-complex extracted into benzene λex = 555 nm, λem = 575 nm	detection limit 12 μg/l	23
Non-Saline Natural Water	U separated from foreign ions by Dowex 1-X8 anion-exchange resin, fluorescence intensity measured after fusion λex = 280 nm, λem = 470-510 nm	detection limit 0.3 μg/l.	24

Table 1.1 Continues...

Sample	Reagent & Conditions	Remarks	Ref.
Natural water	Using FIA techniques. U separated and/or preconcentrated on an activated silica gel column. carrier stream = 1.3 M H_2SO_4/H_3PO_4 $\lambda ex = 325$ nm, $\lambda em = 495$ nm	range 10-250 mg/l	25
Rock	Using FIA techniques. U preconcentrated on a tri-n-octylphosphine oxide/polyethylene column from a carrier stream of 1 M K_2HPO_4 $\lambda ex = 270$ nm, $\lambda em = 494$ nm	range 0.08 - 0.8 mg/l	26

1.2 Yttrium

1.2.1 General (27- 32)

Yttrium was discovered in 1794 in the gadolinite ore [(Be, Fe) Ln_2SiO_{10}] by Gadolin. It has an atomic number of 39 and relative atomic mass of 89. Yttrium has only one stable isotope, Y-89. The electronic structure of yttrium is [Kr] 4 d^1 5 s^2 and it exists in the Y^{3+} oxidation state. Yttrium has a relatively small nuclear charge [Z=39] and forms complexes with ionic radius almost equal to that of holmium. The redox potential of yttrium ($M^{3+}{}_{aq}/M$) is -2.37 V which is comparable to that of some rare earth elements such as dysprosium (-2.35 V) and terbium (-2.39 V). Indeed, yttrium has very similar chemical properties to the lanthanide elements, so although it is not itself a lanthanide (having no f-electrons), it is frequently associated with the lanthanide group.

The lanthanides, also known as the rare earth elements [REE], are a group of 15 elements with atomic number 57-71 which exhibit very similar and physical properties. Mostly the elements occur in the same ores and are difficult to separate from the each other. Yttrium is always present in the more important rare earth ores. The abundance of yttrium in igneous rock is close to zinc and cobalt at about 30-40 grams per tonne.

The rare earth elements are widely distributed in nature and over one hundred types of ore have been found which contain them : the most important of these are Mona zite [(Th, Ln)PO_4] , Gadolinite [(Be, Fe) $Ln_2Si_2O_{10}$] , Xenotime [$LnPO_4$] , Euxenite [(Ln, U, Th) (Nb, Ta, Ti)$_2O_6$] and Bastnaesite [$LnFCO_3$] (Ln = REE). The best source of yttrium is Xenotime which contains 60% Y, 9% Dy, 6% Yb, 5% Er and 10% of other heavy rare earth elements. The lanthanide elements in Xenotime are extracted from ore by treatment with sulfuric acid (acid breakdown) or caustic soda (alkaline breakdown).

Yttrium forms hydrides, oxides, halides, hydroxides, carbonates and nitrates (Fig. 1.2.1). Yttrium oxide and hydroxide are bases strong enough to adsorb carbon dioxide from the atmosphere. Yttrium fluoride is insoluble and precipitates even from strong acidic solution : these properties are used as characteristic tests for yttrium.

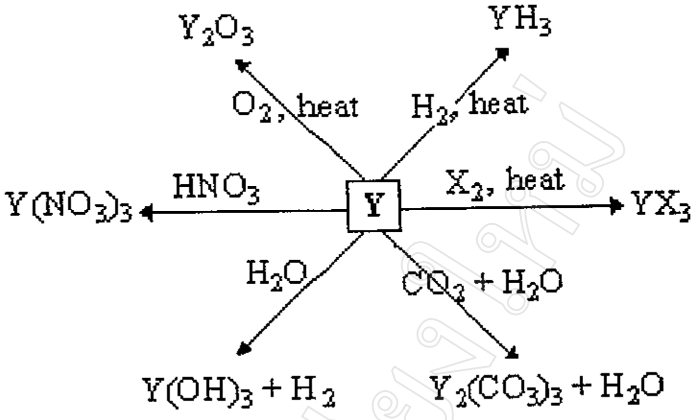

Fig. 1.2.1 Some reactions of yttrium [X=halogen] (29)

1.2.2 Applications of yttrium

Yttrium is important in the field of electronics. It is used in semiconductors and superconductors such as $YBa_2Cu_3O_{7-x}$, a compound which becomes super conducting at 90 K (29). Yttrium in the form of $Y_3Fe_5O_{12}$, a garnet oxide, is used in bubble devices for memory storage and for microwave filters in radar devices. The related $Y_3Al_5O_{12}$ is used as a gemstone and has been used as a substitute for the famous Cartier Diamond (31). Yttrium oxides are sometimes used as sintering aids for producing aluminium nitride ceramics, also as crucible materials (34). Yttrium is also used in the fabrication of special steels. For this purpose, yttrium is not separated entirely, but remains part of the naturally occurring mix with the other lanthanides which is converted to chlorides and then reduced electrolytically to mischmetall, an alloy of a number of rare earth metals, which is added to steels (29).

Yttrium also finds applications in medicine and biotechnology, for example as a marker in nutrition and biochemistry, and for radiotherapy. The neodymium-yttrium-aluminium garnet laser [Nd:YAG laser] is used in cancer therapy and surgery, and is also used as a light source in Raman spectrophotometers.

1.2.3 Determination of yttrium

The chemical properties of yttrium are close to those of the REE and therefore, prior to the determination of yttrium it must be separated from REE which will interfere in the determination. Almost, all methods which have been reported for the determination of yttrium are combined with ion-exchange techniques.

Inductively coupled plasma atomic emission spectrometry [ICP-AES] has been used to determine yttrium in geological silicate materials after preconcentration and separation on Dowex-50WX8 cation exchanger, with linear range of 0.01-100 mg/l and a detection limit of 0.0083 μg/g (34) : yttrium has been similarly determined using AG-50WX8 cation exchanger with a detection limit of 0.2 μg/g (35).

High performance liquid chromatography [HPLC] using a dynamic ion exchange technique has been reported for the determination of yttrium. Dynamic ion exchangers are formed when hydrophobic ions, present in the mobile phase, are sorbed onto the hydrophobic surface of a reversed phase to produce a charged double layer at the surface where ion exchange can occur. These exchangers give improved column efficiency for metal ions and greater flexibility with regard to choice of separation conditions. By using this technique, yttrium in extracts of uranium ore can be determined with a detection limit down to 0.1 mg/l (36).

Gas liquid chromatography [GLC] has been used to determine yttrium. The method is based on the use of β-diketones as ligands for yttrium with extraction into tri-n-butylphosphate followed by determination of the complex by GLC. Yttrium can be determined over a range up to 1.5 x 10^{-5} g of metal with a detection limit of 2 x 10^{-7} g (37). Neutron activation analysis [NAA] has been used to determine yttrium in hot spring water after preconcentration onto magnesium oxide (38).

A techniques which has been used to determine yttrium without separation is inductively coupled plasma optically emission spectrometry [ICP-OES] which has been applied to the determination of yttrium in nickel-base alloys over a concentration range from 10 to at least 2,000 mg/l (39).

X-ray fluorescence [XRF] can also be used to determine yttrium in a solid sample. The sample is fused with a mixture of lithium tetraborate and sodium nitrate to form a glass disk, in which the yttrium is determined by XRF with an accuracy 10% for a concentration between 20 and 100 mg/l and 5% for a concentration of more than 100 mg/l (40). Spectrofluorimetric determinations have also been reported, such as the reaction of yttrium with salicylaldehyde carbohydrazone. The reaction is carried out at pH 6.3 -6.9 with a linear range of 75-600 μg/l of yttrium (41). Yttrium can form a complex with 8-hydroxyquinoline and its dihalide derivatives. The fluorescence determination of yttrium in scandium oxide based on this complex gave was found to give a detection limit of 1×10^{-4} % (42). Yttrium in rare earth silicate ores has been determined by atomic absorption spectrometry [AAS] using lanthanum as an interference suppressor. A detection limit was found 0.3 mg/l (43).

In addition to the various techniques which have been exemplified, spectrophotometry has frequently been used because of its speed, low cost and convenience. The sensitivity has been improved by preconcentrating with ion-exchange resins. Various chromogenic reagents have been used to determine yttrium. Table 1.2 represents a brief review of spectrophotometric yttrium determination.

Table 1.2 Review of yttrium determination by spectrophotometry

Sample	**Reagent & Conditions**	**Linear range**	**Ref.**
cast steel	Arsenazo I, Y co-precipitated with Th^{4+} as fluoride, dissolved in HNO_3+H_3BO_3 and separated from Th^{4+} using Dowex1-X10 anion exchanger. λ 580 nm	up to 100 μg	44
Ni-base alloys	p-nitrochlorophosphonazo, Y forms 1:3 complex in 0.2 M $HClO_4$ solution ε 84900 $l.mol^{-1}.cm^{-1}$, λ 730 nm	0-6 μg /25 ml solution.	45
standard	Alizarin Red S, in acetic/acetate buffer pH 4.7. λ 550 nm	8-80 mg/l	47

Table 1.2 Continues...

Sample	**Reagent & Conditions**	**Linear range**	**Ref.**
synthetic Y + Mg	Pyrocatechol violet, in ascorbic acid + gelatin + ammonium acetate, pH 8.5. ε 26000 $l.mol^{-1}.cm^{-1}$, λ 665 nm	0-1.8 mg/l	46
standard	Naphthazarin in 50% ethanol, Y forms 1:1 complex in 0.1 M $NaClO_4$ at pH 5.5 ε 11500 $l.\ mol^{-1}.cm^{-1}$, λ 595 nm	1.95-8.86 mg/l	48
standard	Quinizarin green, Y forms 1:1 complex in dimethyl formamide 40% v/v + 0.1 M $NaClO_4$, pH 7.7 ε 4600 $l.mol^{-1}.cm^{-1}$, λ 600 nm	2×10^{-5} - 3×10^{-4} M	49
Chromium-base alloys	Arsenazo III, Y separated from Cr^{6+} by precipitation as hydroxide and dissolved in dil. HNO_3, pH 2.5 λ 660 nm	0-100 µg	50
standard	4-(2-pyridylazo) resorcinol, Y forms 1:2 complex at pH 6.2 ε 21000 $l.mol^{-1}.cm^{-1}$, λ 515 nm	0.18-5.96 mg/l	51

Techniques used for the determination of yttrium require normally either time-consuming manipulations, expensive equipment or difficult automation. FIA allows determinations to be carried out more simply and more quickly than by a batchwise method. Some FIA techniques have already been developed to determine yttrium. The brief review of these techniques is given in Table 1.3 .

Table 1.3 FIA techniques for the determination of yttrium

Sample	Reagent & Condition	Remarks	Ref
standard	Xylenol orange + cetylpyridinium bromide in ethanol carrier stream = 0.1 M acetate buffer pH 5.5 λ 600 nm detector = UV-Vis-spectrophotometer	linear range up to 4.5 mg/l	52
standard	Arsenazo III carrier stream = sodium acetate buffer pH 4.0 λ 650 nm detector = UV-Vis-spectrophotometer	linear range 0.02-1 mg/l	55
standard	1-(2-pyridylazo)-2-naphthol + Triton X-100 carrier stream = 0.01 M HBO_2 + $NaBO_2$ buffer pH 9.2. λ 560 nm detector = UV-Vis-spectrophotometer	detection limit 2.1×10^{-7} M	53
synthetic	Trichloroarsenazo + HCl + sodium acetate buffer pH 3 carrier stream = 1 mM CDTA λ 636 nm detector = UV-Vis-spectrophotometer	recovery 90-100 %	54

1.3 Flow Injection Analysis

Flow injection analysis [FIA] was first introduced in 1975 by Stewart, Beecher and Hare in the United States, simultaneously with Ruzicka and Hansen in Denmark (56). FIA is based on the injection of sample into a moving, nonsegmented continuous carrier stream of a suitable liquid. The injected sample forms a zone and the laminar flow present in narrow-bore tubing causes the injected sample to mix with the reagent, and transports it towards a detector, the response of which continuously changes due to the passage of the sample material through the flow cell. It is not necessary for the reaction to reach equilibrium because the extent of reaction is the same for both sample and standard. The basic principle of FIA is based upon sample injection, reproducible timing and controlled dispersion (57).

Preconcentration in FIA

One of the great advantages of FIA is the ease with additional components which can be added to the system to achieve particular analytical objectives. This is most notably exemplified by the incorporation of small packed reactors, which subject an injected sample to appropriate pre-treatment in order to facilitate the detection of the analyte. A packed reactor in an FIA system is designed to perform the same chemistry on each individual sample. Ion exchangers have been employed as column packing materials in order to preconcentrate an analyte, and/or to remove matrix components that might interfere.

FIA preconcentration techniques were originally proposed to enhance the sensitivity of measurement of cationic trace elements in very diluted aqueous samples. After introducing a relatively large volume of sample solution, the analyte content of which is retained on a miniaturised packed reactor incorporated within the FIA channel, the analyte is subsequently released and passed to a detector.

In-valve column preconcentration has been achieved (20) using an ion-exchange column instead of a sample loop. When the valve is in the load position, the sample is preconcentrated. When the valve is turned to the inject position the sample is released from the ion-exchange column by the eluent from the FIA system.

1.4 Aims of the Thesis

The aims of this research work are summarised as follows :

1. To investigate on a flow injection fluorescence analysis for uranium.
2. To investigate on a flow injection spectrophotometric determination of yttrium using an in-valve column.