CHAPTER 1
INTRODUCTION

1.1. General considerations:

Practical significance of ^{99}Mo ($T_{1/2}$ = 2.75 d) comes from its decay product ^{99m}Tc ($T_{1/2}$ =6.01 h) which is the radionuclide of choice for routine diagnostic nuclear medicine. It has favorable physical, chemical, and nuclear properties as well as its daily direct production, from ^{99}Mo/^{99m}Tc generators, in a hospital (**IAEA, 1989; Zykov and Kodina, 1999**). About 80 % of the diagnostic nuclear medicine procedures are performed using ^{99m}Tc labeled compounds (**Nair et al., 1992; Smith et al., 1988; Takekawa et al., 1999; Colak and Akaydin, 2001**). Molybdenum-99 can be produced via ^{235}U(n,f) reaction with a fission yield , Y_f, of 6.11 % (**England and Rider, 1993**).

To minimize the problem of the high-level fission-product radioactive wastes and to maximize the economic benefit, other valuable fission radioisotopes should be separated and utilized in different applications (e.g., medical, industrial, etc). **Salacz (1989)** illustrated a production program of ^{99}Mo, ^{131}I, and ^{133}Xe at the Institut National des Radioéléments (IRE) in Belgium by irradiation and reprocessing of uranium targets. Also, in Nuclear Energy Corporation of South Africa (NECSA), ^{99}Mo and ^{131}I are produced in the same processing procedure (**IAEA, 2003**). The radioisotopes of ^{131}I ($T_{1/2}$ = 8.04 d; Y_f= 2.89 %), ^{103}Ru ($T_{1/2}$ = 39.27 d; Y_f= 3.03 %), ^{106}Ru ($T_{1/2}$ = 1.02 y; Y_f= 0.402 %), ^{137}Cs ($T_{1/2}$ = 30.07 y; Y_f= 6.19 %), ^{95}Zr ($T_{1/2}$ = 64.02 d; Y_f= 6.5 %), and ^{95}Nb ($T_{1/2}$ = 34.97 d; Y_f = 6.5 %) (**England and Rider, 1993**) have a great contribution to the radioactivity level of the ^{235}U-fission products and are the main contaminants of the ^{99}Mo product. It will be advantageous to separate them as beneficial fission-product radionuclides, in the production process of ^{99}Mo, and to reduce the gamma-radioactivity level of the remaining waste solution.

It is possible to separate long-lived fission-radioisotopes such as ^{106}Ru and ^{137}Cs from irradiated uranium targets or their nuclear waste solutions aged for ≥ 2 y but with the loss of many other short- and intermediate-lived fission-radioisotopes, such as ^{99}Mo ($T_{1/2}$ = 2.75 d), ^{131}I ($T_{1/2}$ = 8.04 d), ^{140}Ba ($T_{1/2}$ = 12.75 d), ^{140}La ($T_{1/2}$ = 1.68 d), ^{141}Ce ($T_{1/2}$ = 32.5 d), ^{95}Zr ($T_{1/2}$ = 64.02 d), and ^{95}Nb ($T_{1/2}$ = 34.97 d), etc. Generally, analytical and identification problems are more complicated in the processing of hot irradiated uranium targets compared with aged ones. So that to establish standard radiochemical separation method(s) of fission radioinuclides from hot uranium targets, it is important to try similar and/or modified method(s) applied with aged uranium targets. The essentially obtained analytical and identification data will enhance quality control investigations of the separated radionuclides.

1.2. Chemistry, radiochemistry and nuclear chemistry of uranium:

1.2.1. Chemistry of uranium:

Uranium is a member of the actinide series. It is a highly reactive metal. It forms intermetallic compounds with many other metals such as Al, Be, Bi, Co, Cu, Ga, Au, Fe, Pb, Mn, Zr, and Nb. Uranium combines with most elements to form a large variety of compounds (**Gindler, 1962**). In its compounds, uranium shows oxidation numbers of +2, +3, +4, +5, and +6. UO and US are compounds of divalent uranium. Trivalent uranium compounds include UF_3, UBr_3, UI_3, and UH_3. Complex salts such as $3(CN_3H_6)_2CO_3.U(CO_3)_2.4H_2O$ and $2(NH_4)_2C_2O_4.U(C_2O_4)_2.6H_2O$ form important uranium (IV) compounds. UF_5, UCl_5, $UCl_5.SOCl_2$, and $UCl_5.PCl_5$ are examples of pentavalent uranium compounds. Hexavalent uranium is represented by UF_6, UCl_6, uranates, and uranyl (UO_2^{2+}) compounds (**Bradley et al., 1957; Gindler, 1962**).

Uranyl compounds are the most numerous uranium compounds and vary in type from simple salts, e.g., $UO_2(NO_3)_2$, to complex organic arrangements, e.g., $UO_2(NO_3)_2.2CH_3COC_4H_9$. Complex salts of uranyl ion with arsenate,

chromate, and vanadate are also known (**Gindler, 1962; Cordfunke, 1969**).

Uranates and peruranates are important compounds in the analytical chemistry of uranium. Uranates have the general formula $xM_2^{I}O.yUO_3$ or $xM^{II}O.yUO_3$. They may be prepared by different methods. However, in usual analytical procedures, they are precipitated from a uranyl solution by the addition of a hydroxide solution, e.g., NH_4OH, NaOH, $Ca(OH)_2$ etc. The uranates are insoluble in water but dissolve in acids (**Etherington, 1958; Gindler, 1962**).

UO_2 (brown-black), U_3O_8 (greenish black), and UO_3 (orange-yellow) are important oxides of uranium. The oxide UO_3 is soluble in most acids forming solutions which contain the yellow linear $[O=U=O]^{2+}$ ion or its complexes. Reduction of U_3O_8 with hydrogen at 600 °C yields UO_2 (**Sharpe, 1984**).

1.2.2. Radiochemistry and nuclear chemistry of uranium:

Natural uranium contains three radioactive isotopes; ^{234}U ($T_{1/2}$ = 2.47 × 10^5 y), ^{235}U ($T_{1/2}$ = 7.04 × 10^8 y), and ^{238}U ($T_{1/2}$ = 4.47 × 10^9 y) with isotopic abundances of 0.0055, 0.72, and 99.27 %, respectively (**Baglin and Chu, 1998**).

When uranium is irradiated in a thermal neutron flux, ^{235}U undergoes a neutron-induced fission with a cross section of 585 barn (**Glasstone, 1955; Ehman and Vance, 1991; Arora and Singh, 1994; Baglin and Chu, 1998**). Binary fission reaction of ^{235}U induced by thermal neutrons can be written in the following form:

$$n + {}^{235}U \longrightarrow {}^{236}U^* \longrightarrow (A_1,Z_1) + (A_2,Z_2) + Nn + \gamma\text{'s}$$

This form indicates the formation of the unstable $^{236}U^*$ nucleus, which subsequently splits into two fragments of atomic masses A_1 and A_2, respectively, with the release of N neutrons (N = 2 or 3) and gamma rays. In this form, the emission of additional particles, most notably α particles, is ignored.