# PART 1

# SEPARATION AND DETERMINATION OF Zr(IV) AND Hf(IV) AS TERNARY COMPLEXES BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

# CHAPTER 1

# INTRODUCTION

## 1.1 History and chemistry of zirconium and hafnium

Elemental zirconium (Zr), meaning gold colored, was first by identified and named in 1789 by the German chemist M.H. Klaproth. Hafnium (Hf) is chemically similar to zirconium that it was in 1923, when D. Coster and A.K. von Hevesy detected it by using x-ray spectrographic analysis. Zr and Hf are transition elements with atomic number of 40 and 72, respectively, and both are in Group IV of the periodic table. Both metals have very similar chemical and physical properties due to their similar ionic radii (Zr = 0.72A$^o$ and H f = 0.71A$^o$) and the same oxidation states ($Zr^{4+}$ and $Hf^{4+}$) (Klein, 1999). Zr and Hf occur most commonly in nature as the silicate mineral [zircon ($ZrSiO_4$)] and less commonly as baddeleyite [zirconia ($ZrO_2$)]. Although its theoretical chemical formula is $ZrSiO_4$, naturally occurring zircon always contains some hafnium, commonly around 2% (as $HfO_2$) but it can be as high as 4% (Kogel, 2006; Merian, 1991).

## 1.2 Importance

Determination of Zr and Hf in various matrixes is important in both industrial and geological applications. In industrial fields, Zr find important applications in the nuclear industry, ceramics, refractories, television glass, enamels, foundry molds and abrasive grits. Some chemical processing industries use zirconium metal for corrosion-resistant vessels and piping. Hf as a by-product from Zr has been found to be a good absorber of neutrons, its use as a moderator in control rods for nuclear reactors. It is also used in the manufacture of the filaments for electric light bulbs and alloys. (Kogel, 2006; Merian, 1991).

In geochemistry, Zr and Hf are extremely important traces to understand the evolution of Earth's major crustal and mantle reservoirs (Yang, 2002). Zr is widely distributed in Earth's crust but not in very concentrated deposits. Zr is a common accessory mineral in granite rocks and basalts. It is one of the earliest minerals to crystallize from cooling magma. Zircon can also occur as a gemstone and has been recognized as a semiprecious stone since biblical times (Kogel, 2006). Due to their similar ionic radii and valency states, Zr and Hf generally show extremely similar geochemical behavior and have a constant ratio of chondritic value (~36.3) in mantle and mantle derived rocks (Table A in Appendix A). However, Zr/Hf ratio showed in igneous rocks to vary over the range of 2.5 to 335 (Dostal, 2000; Hui, 2011). The background levels of Zr in rocks at the low ppm levels and Hf at sub-ppm levels.

### 1.3 Current analytical techniques of Zr(IV) and Hf(IV)

Several analytical methods have been used to determine trace amounts of Zr and Hf in geological materials. These include X-ray emission spectrometry (Abdel-Gawad, 1996), Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) (Reid, 1999), multivariate spectrofluorimetry assisted by several chemometrics methods (Wang, 2000), extraction chromatography and inductively coupled plasma mass spectrometry (ICP-MS) (Yang, 2002), ICP optical emission spectrometry (ICP-OES) after cloud point extraction (S. Shariati, & Yamini, Y, 2006; S. Shariati, Yamini, Y., & Zanjani, M.K, 2008), ICP-MS using lithium metaborate fusion digestion (Roy, 2007) and ICP-MS after Tm addition and alkaline fusion (Bayon, 2009). The major disadvantage of these methods is high cost of the instrumentation.

### 1.4 Separation of Zr(IV) and Hf(IV) using metallochromic ligands

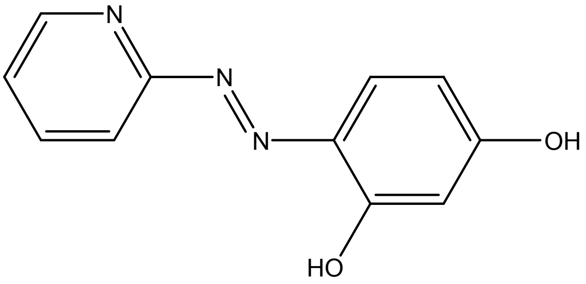
There are several previous reports of the use of metallochromic reagents for binary and ternary complexes with metal ions such as Zr(IV) and Hf(IV). Those metallochromic reagents were 4-(2-pyridylazo)resorcinol (PAR) (Kalyanaraman, 1983), 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (Br-PADAP) (Rathaiah, 1986, 1988), tetrahydroxyazon SC (Uysal, 2011) and xylenol orange (Kate, 1998).

The pre-column formation of ternary complexes with metallochromic reagents and auxiliary agents of metal ions give more sensitive and selective results than binary complexes. For example, using RP-HPLC methods to determine vanadium as ternary complexes with PAR and auxiliary agents (hydroxylamine ($NH_2OH$), tartrate, citrate and hydrogen peroxide ($H_2O_2$)) (V. Narumol, Dicinoski, G.W., Townsend, A.T., & Haddad, P.R, 2002; S. Oszwaldowski, & Jarosz, M, 1997). These methods were more selective with V(V) than V(IV) and produced good separation from other elements. In addition, Br-PADAP and fluoride were used as metallochromic reagent and auxiliary ligand for ternary complexes with uranium (U(VI)) (S. Oszwaldowski, Połeć, K., & Jarosz, M, 2000).

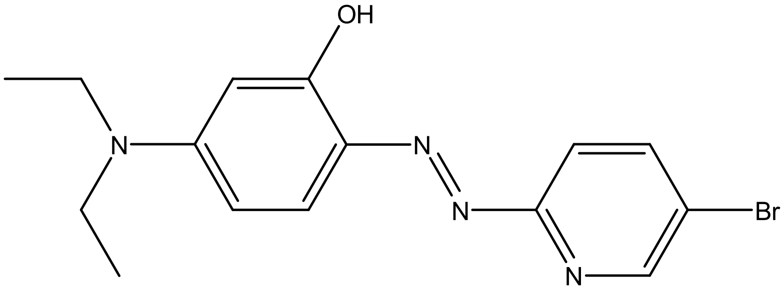
Another example, niobium (Nb) and tantalum (Ta) has very similar ionic radii (Nb = 0.64A$^o$ and Ta = 0.64A$^o$) and the same oxidation states ($Nb^{5+}$ and $Ta^{5+}$) (Hui, 2011). The simultaneous determination of Nb(V) and Ta(V) is very difficult due to the great similarity of their behavior. In the previous reported, using RP-HPLC method for the determination of Nb(V) and Ta(V) in geological samples by the separation of ternary complexes of the metal ions with PAR and citrate (V. Narumol, Doble, P., & Haddad, P.R, 2000b; V. Narumol, Macka, M., Paull, B., Münker, C., & Haddad, P.R, 1999), Br-PADAP and citrate (V. Narumol, Doble, P., Yu, Z.S., & Haddad, P.R, 1999) and 2-(5-bromo-2-pyridylazo)-5-[N-propyl-N-(3-sulfopropyl) amino]phenol (Br-PAPS) and citrate (V. Narumol, Doble, P., & Haddad, P.R, 2000a). These methods provided good separation of Nb(V) and Ta(V) from other elements and also gave high sensitivity.

The simultaneous determination of Zr(IV) and Hf(IV) is extremely difficult due to the great similarity of their behavior. The previously reported method used pre-column formation of ternary complexes of Zr(IV) and Hf(IV) with Br-PADAP and fluoride, and their separation was done by the RP-HPLC method (S. Oszwaldowski, & Jakubowska, J, 2003; S. Oszwaldowski, Lipka, R., & Jarosz, M, 1998). This RP-HPLC method (S. Oszwaldowski, Lipka, R., & Jarosz, M, 1998) provided high sensitivity, (DL = 0.8 and 0.2 µg $L^{-1}$ for Hf(IV) and Zr(IV), respectively) but gave the analysis time in 15 minutes. However, using solid phase extraction (SPE) along with RP-HPLC (S. Oszwaldowski, & Jakubowska, J, 2003) for the determination of Zr(IV) and Hf(IV) in reference rock was found to increase sensitivity (DL = 0.2 and 0.53 µg $L^{-1}$ for Hf(IV) and Zr(IV), respectively) but has an interference peak with Zr(IV) from using SPE.

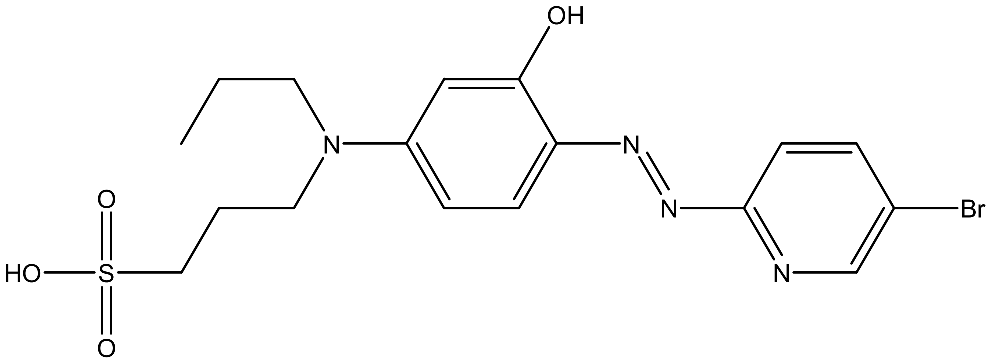
To find an alternative method for separation of Zr(IV) and Hf(IV) in rock sample, the short analysis time and high selectivity HPLC method is required. Figure 1.1 shows structure of PAR, Br-PADAP and PAPS, it can be seen Br-PAPS to provide a better solubility characteristics than Br-PADAP and higher sensitivity than PAR. Thus, Br-PAPS was chosen as metallochromic reagent for complex formation.



4-(2-pyridylazo)-resorcinol or PAR



2-(5-bromo-2-pyridylazo)-5-(diethylamino)phenol or PADAP



2-(5-bromo-2-pyridylazo)-5-[*N*-propyl-N-(3-sulfopropyl)amino]phenol or PAPS

Figure 1.1 Structure of azo dye: PAR, Br-PADAP and Br-PAPS

## 1.5 Aim of this research

The aim of the present research was to develop the RP-HPLC for the determination of Zr(IV) and Hf(IV) by using Br-PAPS and fluoride for ternary complex formation. The developed method was applied to determine both metals in real rock sample.