CHAPTER I

INTRODUCTION

1.1 Statement of the problem

Chromium is an element present in the aqueous environment mainly in +3 and +6 oxidation states. Its toxicity and reactivity depend on numerous factors, e.g. chemical form, pH and adsorption pathway. Cr(III) compounds are sparingly soluble in water, while Cr(VI) species are readily soluble, which may result in enhancing Cr(VI) level in water sources. Cr(III) is non-toxic element. It is an essential species to mammals for their maintenance of glucose, lipid and protein metabolism, and is therefore essential for human health in trace concentration [1-3]. On the other hand, Cr(VI) is extremely toxic to humans since it is a potentially carcinogenic agent [4-6]. Chromium species can enter the environment from industrial effluent or waste disposal sources such as waste water from steel works, electroplating and tanning industries [1, 7].

The measurement of the total quantity of an element cannot be used to determine the actual environmental impact. The methods which give the total amount of an element in a sample and the methods which give the structural information on the chemical form of the element, the concept of speciation analysis has been developed. Speciation, defined as the quantification of the different chemical forms of an element, has therefore become an important topic of present-day analytical research [8-11].

Generally, chromium speciation analysis is tended to be indirect method or changing form method. Cr(III) is oxidized to Cr(VI) using oxidizing agent such as H_2O_2 and $KMnO_4$ while Na_2SO_3 is used as the reducing agent for the reduction of Cr(VI) to

Cr(III). This method is operated in two steps. First, the selective determination of one chromium species is carried out using a suitable technique such as UV-Visible spectrophotometry, atomic absorption spectrometry, etc. The second step is the changing form of the other chromium species to the same form of the species in the first step using suitable reagent followed by a suitable determination technique given the total amount of chromium. The quantity of the other species will be calculated by subtracting the content of the species in the first step from the total chromium content in the second step. However, this method has some disadvantages due to incompleteness in oxidation and reduction. Moreover, the direct determination of chromium in water may not be possible because of matrix interferences, and the low concentrations of chromium in natural water is not compatible with the detection limit of instruments. Therefore, the preconcentration method is required. A well designed preconcentration step may not only concentrate the analyte, but at the same time may also remove interfering species. There are many techniques that can be employed for preconcentration, e.g. co-precipitation, solvent extraction, electrodeposition, membrane extraction and solid-phase extraction (SPE). Solid-phase extraction offers a number of important benefits. It reduces solvent use, solvent exposure, disposal costs and extraction time for sample preparation step. In SPE, solid sorbent is an important factor because its selectivity and capacity depend on the types of sorbents. In this research, the sorbent which is chemically modified silica gel with selective ligands is developed. Silica gel is a good solid support because of its thermal, chemical and mechanical stability. Since there are a large number of the reactive sites on the silica gel, a large number of immobilized ligand can be modified resulting to good sorption capacity for analytes. Therefore, it is possible to improve the selectivity of the modified silica gel by selecting the appropriated ligand in the modification.

There are many reports on the use of SPE in chromium speciation analysis [3, 5, 12-17], but these works still have several steps in the sample pretreatment such as the changing form of chromium and the adjusting pH of the solution. In addition,

preconcentration normally involves extra manipulations of the sample and additional reagents leading to a bad effect on sample contamination and/or loss. Therefore, this research is developed to minimize these problems.

1.2 Objectives and scope of the research

The objectives of this research are to study the adsorption properties of two chemically modified silica gels with amidoxime and benzothiazolyl moieties (namely Si-Amidoxime and Si-Benzothiazole, respectively), and to develop a method for preconcentration and speciation of chromium in aqueous solution using Si-Amidoxime and Si-Benzothiazole as solid sorbents followed by flame atomic absorption for chromium determination. The structures of Si-Amidoxime and Si-Benzothiazole are illustrated in Figure 1.1.

Si-Amidoxime   **Si-Benzothiazole**
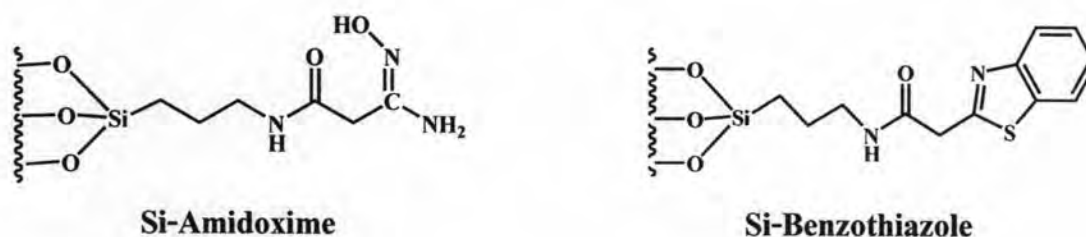
Figure 1.1 Structures of Si-Amidoxime and Si-Benzothiazole

The optimization for retention of Cr(III) and Cr(VI) using batch and column methods were carried out. Several parameters such as pH of solution, contact time, type of eluent, sorption capacity, flow rate, sample volume including the effect of interfering ions were investigated. The optimum condition was employed for preconcentration and speciation of Cr(III) and Cr(VI) using column method. Finally, the proposed

preconcentration and speciation procedure was validated by the use of spiked synthetic solution and spiked real sample.

1.3 The benefits of this research

In this research, a method for simultaneous preconcentration and speciation analysis of chromium in an aqueous solution was achieved using benzothiazolyl and amidoxime modified silica gel as solid sorbents with the reduction of sample pretreatment step.