CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Chemistry of chromium

Chromium exists in oxidation states ranging from +6 to -2, however, only the +6 and +3 oxidation states are commonly encountered in the environment. Cr(VI) exists in solution as monomeric ions H_2CrO_4, $HCrO_4^-$ (bichromate), and CrO_4^{2-} (chromate), or as the dimeric ion $Cr_2O_7^{2-}$ (dichromate). The monomeric species impart a yellow color to the water when the concentration of Cr(VI) is greater than 1 mg L^{-1}. Water that contains high levels of $Cr_2O_7^{2-}$ has an orange color [18-21].

The monomeric chromate species are related to a series of acid dissociation reactions [22] as follows:

$$H_2CrO_4 \rightleftharpoons H^+ + HCrO_4^- \qquad K_1 = 1.21$$

$$HCrO_4^- \rightleftharpoons H^+ + CrO_4^{2-} \qquad K_2 = 3.0\times10^{-7}$$

The dichromate is the result of the polymerization of the monomeric bichromate ions to form the dimer, $Cr_2O_7^{2-}$, as follows:

$$2HCrO_4^- \rightleftharpoons Cr_2O_7^{2-} + H_2O \qquad K_3 = 35.5$$

$$HCr_2O_7^- \rightleftharpoons H^+ + Cr_2O_7^{2-} \qquad K_4 = 0.85$$

Cr(VI) can also exist in two other forms but the concentrations are considered too low to be significant. The reactions to produce these forms are shown in equations as follows:

$$Cr_2O_7^{2-} + H^+ + HCrO_4^- \rightleftharpoons Cr_3O_{10}^{2-} + H_2O$$

$$Cr_3O_{10}^{2-} + H^+ + HCrO_4^- \rightleftharpoons Cr_4O_{13}^{2-} + H_2O$$

Disregarding to chromium in the form of $Cr_3O_{10}^{2-}$ and $Cr_4O_{13}^{2-}$, the total concentration of chromium in a closed system is given by equation 2.1.

$$[Cr] = [H_2CrO_4] + [HCrO_4^-] + [CrO_4^{2-}] + \frac{1}{2}[Cr_2O_7^{2-}] + \frac{1}{2}[HCr_2O_7^-] \quad (2.1)$$

The complete mathematical derivations for calculating the concentrations of various chromium species within the range of our experimental conditions (at a specific total concentration of Cr(VI) and at different pH of the equilibrium solution) have been presented in Appendix A.

The relative concentration of each species depends on both the pH of solution and the total concentration of Cr(VI), illustrated in Figure 2.1 and Figure 2.2, respectively. Significant concentration of H_2CrO_4 only occur under the extreme condition of pH 1. Above pH 6.5, CrO_4^{2-} generally dominates. Below pH 6.5, $HCrO_4^-$ dominates when the Cr(VI) concentration is low (< 30 mM), but $Cr_2O_7^{2-}$ becomes significant when the total Cr(VI) concentration is greater than 30 mM [18].

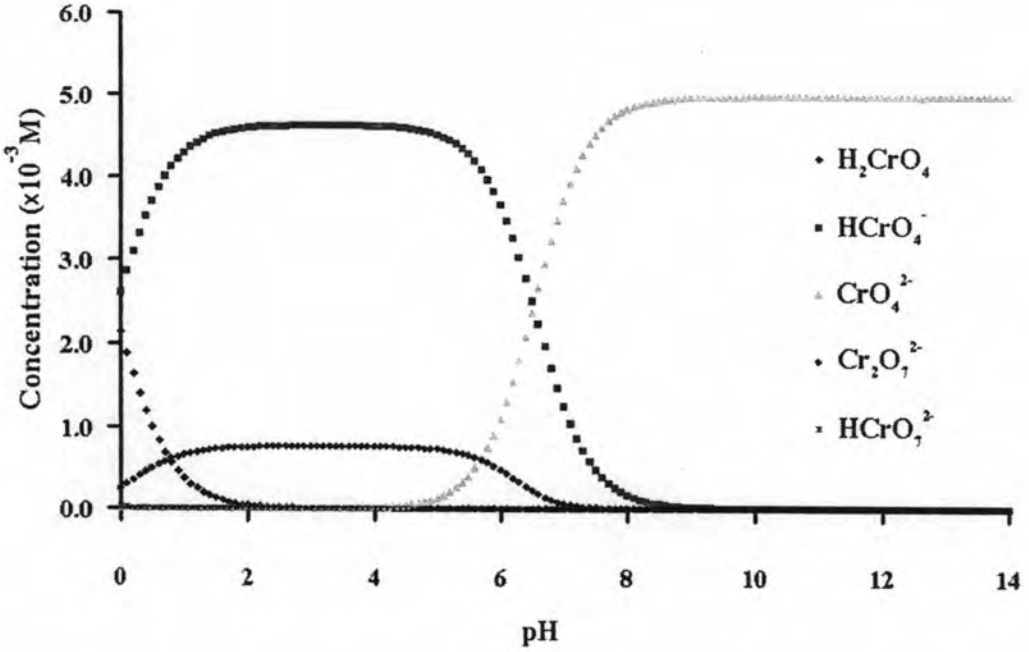

Figure 2.1 Distribution of Cr(VI) species as a function of pH (Total concentration = 0.005 M)

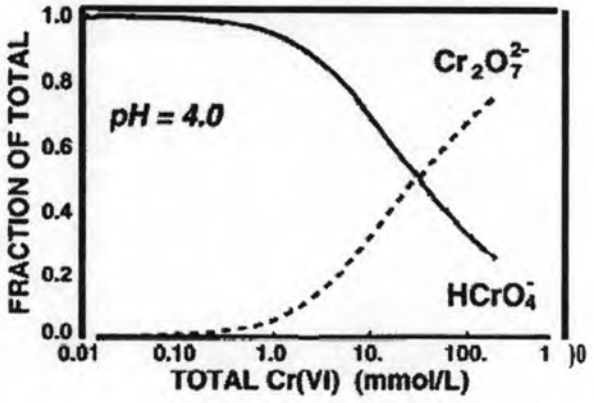

Figure 2.2 Fraction of bichromate ($HCrO_4^-$) and dichromate ($Cr_2O_7^{2-}$) at pH 4 as a function of the total Cr(VI) concentration [18]

In the Cr(III)-H_2O system, Cr(III) exists predominantly as Cr^{3+} below pH 3.5. With increasing pH, hydrolysis of Cr^{3+} yields $Cr(OH)^{2+}$, $Cr(OH)_2^+$, $Cr(OH)_3$, $Cr(OH)_4^-$, $Cr_2(OH)_2^{4+}$, $Cr_2(OH)_3^{3+}$, $Cr_3(OH)_4^{5+}$, $Cr_3(OH)_5^{4+}$ and $Cr_4(OH)_6^{6+}$. At high concentration,

these ions impart a green color to the solution. Under slightly acidic to alkaline conditions, Cr(III) can precipitate as an amorphous chromium hydroxide.

The dominant species from pH 3 to 14 are the Cr-hydroxocomplexes, $Cr(OH)^{2+}$ $Cr(OH)_3$, $Cr(OH)_4^-$, $Cr_2(OH)_2^{4+}$ and $Cr_3(OH)_4^{5+}$ as governed by the following pH-dependent equilibria [23-25]:

$$Cr(OH)_{3\,(s)} + H^+ \rightleftharpoons Cr(OH)^{2+}{}_{(aq)} + H_2O \quad K_5 = -5.80$$

$$Cr(OH)_{3\,(s)} \rightleftharpoons Cr(OH)_{3\,(aq)} \quad K_6 = 7.13$$

$$Cr(OH)_{3\,(s)} + H_2O \rightleftharpoons Cr(OH)_{4\,(aq)}^- + H^+ \quad K_7 = 18.15$$

$$Cr(OH)^{2+}{}_{(aq)} + Cr(OH)^{2+}{}_{(aq)} \rightleftharpoons Cr_2(OH)_2^{4+}{}_{(aq)} \quad K_8 = 3.3$$

$$Cr(OH)^{2+}{}_{(aq)} + Cr_2(OH)_3^{3+}{}_{(aq)} \rightleftharpoons Cr_3(OH)_4^{5+}{}_{(aq)} \quad K_9 = 4.5$$

The hydrolysis behavior of Cr^{3+} is complicated by the slow kinetics of its polymerization reaction [24, 26-27], moreover the polynuclear species of $Cr_2(OH)_2^{4+}$ and $Cr_3(OH)_4^{5+}$ form slowly at 25 °C. Figure 2.3 shows the predicted distribution of Cr(III) hydrolysis species when no other complexing agents are present.

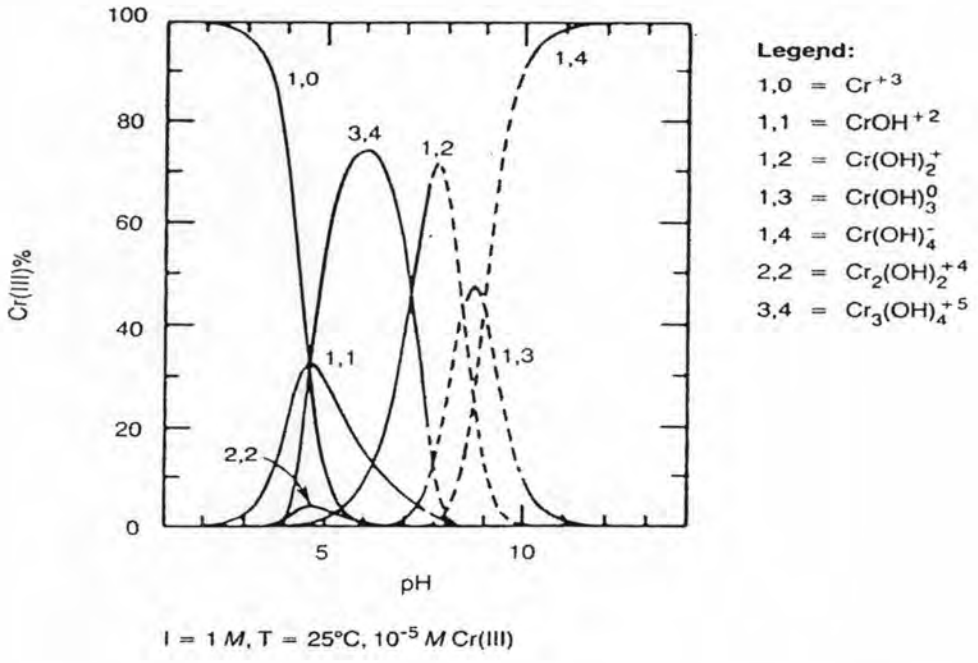

Figure 2.3 Distribution of Cr(III) species as a function of pH [28]

2.2 Solid-phase extraction

Solid-phase extraction (SPE) [12] is a method of sample preparation that concentrates and purifies analytes from solution by sorption onto a disposable solid sorbent, followed by the elution of the analyte with an appropriate eluent for instrumental analysis. Traditionally, sample preparation consists of sample dissolution, purification, and extraction that are carried out with liquid-liquid extraction (LLE). The disadvantages of liquid-liquid extraction include the use of large volume of organic solvent, cumber some glassware, and cost. Furthermore, liquid-liquid extraction often creates emulsions with aqueous samples that are difficult to extract, and therefore, is not easily automated. These difficulties can be overcome with solid-phase extraction.

Initially, SPE was based on the use of polymeric sorbent, such as XAD resins (polymeric sorbents), which were packed in small disposable columns for use on a drug analysis. The early environmental applications consisted of both XAD resins and bonded-phase sorbents, such as C-18. These pre-columns were used for sample trace enrichment prior to liquid chromatography.

2.2.1 Basic principles

SPE method always consists of three to four successive steps: conditioning, loading, washing, and eluting as illustrated in Figure 2.4. In each step, many parameters influence the efficiency of the SPE.

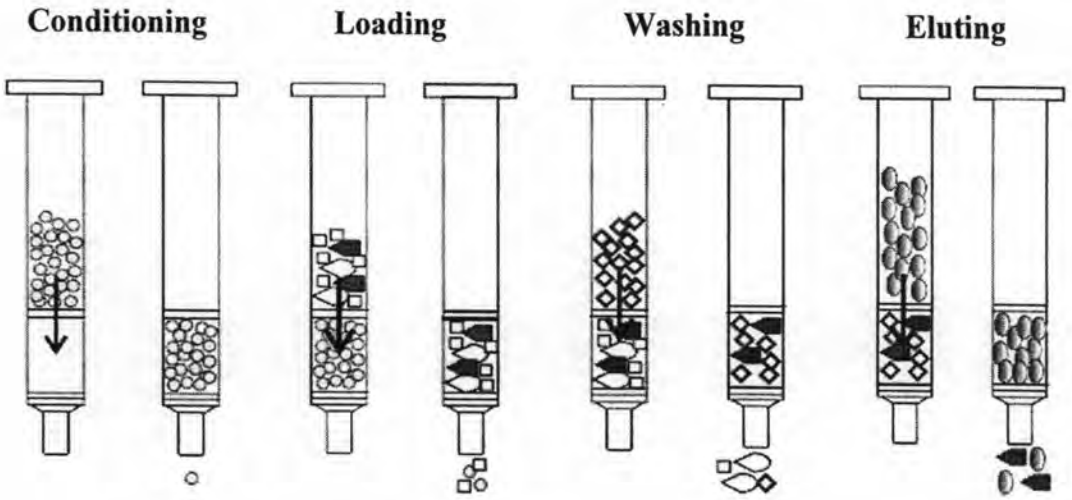

Figure 2.4 SPE operation steps [29]

- Conditioning step

The nature of the conditioning solvent must be appropriate to the nature of the solid sorbent to ensure a good wettability of the functional groups. The sorbent should further be conditioned by a solvent whose nature is similar to that of the sample. Thus, for aqueous samples, the solvent will be water with a pH and ionic strength similar to that of the sample. This step can remove possible impurities initially contained in the sorbent or the packing.

- Loading step

This step is the percolation of the sample through the solid sorbent. An important parameter to control in SPE is the breakthrough volume, which is the maximum sample volume that should be percolated through a given mass of sorbent after which analytes start to elute from the sorbent resulting to non-quantitative recoveries. Depending on the system used, volumes can range from 1 mL to 1 L. The sample may be applied to the column by gravity, pumping, aspirated by vacuum or by an automated system. The sample pH is of prime importance for efficient retention of the trace elements on the sorbents. Its influence strongly depends on the nature of the sorbent used. The sample flow rate should be optimized to ensure the quantitative retention along with minimization of the

time required for sample processing. Even though matrix components may also be retained by the solid sorbent, some of them pass through, thus enabling some purification (matrix separation) of the sample. During this step, the analytes are concentrated on the sorbent.

- Washing step

This step is the washing of the solid sorbent with an appropriate solvent, having low elution strength, to eliminate matrix components that have been retained by the solid sorbent, without displacing the analytes.

- Eluting step

The final step consists of the elution of the analytes of interest by an appropriate solvent. The eluting solvent should be carefully chosen to ensure efficient recovery of the retained target species as far as possible and be compatible with the analysis technique. The solvent volume should be as low as possible in order to obtain a high concentration of analytes but it should ensure the complete elution of the analytes. In addition, the flow rate should be correctly adjusted to ensure efficient elution.

2.2.2 Retention mechanism of elements on the sorbent

The mechanism of retention depends on the nature of the sorbent, including simple adsorption, chelation or ion-exchange. Also, for trace elements, ion-pair solid-phase extraction may be used.

- Adsorption

Trace elements are usually adsorbed on a solid sorbent through van der Waals forces or hydrophobic interaction, which occurs when the solid sorbent is highly non-polar (reversed phase). The most common sorbent of this type is octadecyl-bonded silica (C_{18}-silica). Recently, polymeric reversed sorbent have emerged, especially the styrene-

divinylbenzene copolymer that provides additional π-π interaction when π-electrons are present in the analyte. However, because most trace element species are ionic, they will not be retained by such sorbents.

- Chelation

Several functional groups are capable of chelating trace elements. The atoms most frequently used are nitrogen (e.g. N present in amines, azo groups, amides, nitriles), oxygen (e.g. O present in carboxylic, hydroxyl, phenolic, ether, carbonyl, phosphoryl groups) and sulfur (e.g. S present in thiols, thiocarbamates, thioethers). The nature of functional group will give an idea of the selectivity of the ligand towards trace elements.

Chelating agents may be directly added to the sample for chelating trace elements, the chelates being further retained on an appropriate sorbent. An alternative is to introduce the functional chelating group into the sorbent. For this purpose, three different means are available:

(1) synthesis of new sorbents containing such groups (*new sorbents*),

(2) chemical bonding of such groups on existing sorbents (*functionalized sorbents*),

(3) physical binding of the groups on the sorbent by impregnating the solid matrix with a solution containing the chelating ligand (*impregnated, coated or loaded sorbents*).

The latter remains the most simple to be used in practice, but its main drawback is the possible flush of the chelating agent out of the solid sorbent during sample percolation or elution that reduces the lifetime of the impregnated sorbent.

Binding of metal ions to the chelate functional group is dependent on several factors:

(1) nature, charge and size of the metal ion,

(2) nature of the donor atoms present in the ligand,

(3) buffering conditions which favor certain metal extraction and binding to active donor or groups,

(4) nature of the solid support (e.g. degree of cross-linkage for a polymer).

- Ion-pairing

When a non-polar sorbent is to be used, an ion-pair reagent can be added to the sorbent. Such reagents contain a non-polar portion (such as a long aliphatic hydrocarbon chain) and a polar portion (such as acid or base). The non-polar portion interacts with the reversed-phased non-polar sorbent, while the polar portion forms an ion-pair with the ionic species present in the matrix (that could be either free metallic species in solution or complexes).

- Ion-exchange

Ion-exchange sorbents usually contain cationic or anionic functional groups that can exchange the associated counter-ion. Strong and weak sites refer to the fact that strong sites are always present as ion-exchange sites at any pH such as sulfonic acid groups (cation-exchange) and quaternary amines (anion-exchange), while weak sites are only ion-exchange sites at pH values greater or less than their pK_a such as carboxylic acid groups (cation-exchange) or primary, secondary and tertiary amines (anion-exchange). These groups can be chemically bound to silica gel or polymers (usually a styrene-divinylbenzene copolymer), allowing a wider pH range.

2.2.3 Selection of solid sorbent

The nature and properties of the sorbent are of prime importance for effective retention of metallic species. Careful choice of the sorbent is thus crucial to development of SPE methodology. In practice, the main requirements for a solid sorbent are:

(1) the possibility to extract a large number of trace elements over a wide pH range (along with selectivity towards major ions),

(2) the fast and quantitative sorption and elution,

(3) High capacity,

(4) regenerability,

(5) accessibility.

In particular, sorbents that allow fast reaction rates are preferred to achieve faster extraction as well as higher loading capacity. Hence, sorbents based on hydrophilic macroporous polymers and cellulose or fibrous materials provide excellent kinetic properties. [30]

The broad variety of sorbents available explains one of the most powerful aspects of SPE, which is selectivity. Sorbents can be mainly categorized into inorganic based ones (silica gel SiO_2, alumina Al_2O_3, magnesia MgO and other oxide species) and organic based ones (natural polymers, as well as synthetic polymers), as given in Table 2.1.

Table 2.1 Type of based sorbent and their advantages, disadvantages

Type of based sorbent	Remarks
Inorganic based sorbents	
Silica gel	present the advantages of mechanical, thermal and chemical stability under various conditions, high selectivity towards a given metal ion but suffer from different chemical limitations, namely the presence of residual surface silanol groups and a narrow pH stability range.
Other inorganic oxides	may be influenced by the presence of salts in the matrix. In particular, high concentrations of phosphates and sulfates may decrease trace element retention on titanium dioxide (TiO_2). On the opposite, major cations (Na^+, K^+, Ca^{2+} and Mg^{2+}) are weakly adsorbed on TiO_2.

Table 2.1 *(continue).*

Type of based sorbent	Remarks
Organic based sorbents	
Polystyrene-divinylbenzene based sorbents (PS-DVB)	Amberlite XAD series: highly hydrophobic character and no ion-exchange capacity, hydrophobic character.
Divinylbenzene-vinylpyrro - lidone copolymers(DVB-VP)	determine polar organic compounds in water samples, can dry out during the extraction procedure without reducing its ability to retain analytes, stable over the entire pH range, but no application related to the preconcentration of trace elements.
Carbon sorbents	large surface areas (300-1000 m^2/g), well-recognized for their very strong sorption both for trace organic compounds and trace elements, be retained on this sorbent after addition of a proper chelating agent to the sample such as amino acids, dithizone. Main drawback: their heterogeneous surface with active functional groups often leads to low reproducibility, very reactive and can act as catalysts for oxidation and other chemical reactions.

2.3 Speciation analysis

2.3.1 The meaning of speciation

According to the official definition which is currently under discussion at IUPAC [8-9], speciation analysis is the process leading to the identification and determination of the different chemical and physical forms of an element existing in a sample. Although this definition tends to restrict the term of speciation to the state of distribution of an element among different chemical species in a sample, in practice the use of this term is much wider, specifying either the transformation and/or the distribution of species, or the analytical activities that identify chemical species and measure their distribution.

2.3.2 Main types of speciation

Generally, speciation analysis plays an unique role in studies of biogeochemical cycle of chemical compounds, determination of toxicity and ecotoxicity of selected elements, quality control of food products, control of medicines and pharmaceutical products, technological process control, research on the impact of technological installation on the environment, examination of occupational exposure, and clinical analysis.

The examples of main application areas of speciation analysis are given in Table 2.2.

Table 2.2 Examples of main application areas of speciation analysis [8]

Element	Application area of speciation analysis
Aluminium Al	Polymerization products. Forms of aluminum (e.g. labile, complexed) in serum. Forms of aluminum in food products.
Antimony Sb	Redox forms and organoantimony compounds in the environment and food products.
Arsenic As	Redox forms and organoarsenic compounds in the environment. Aresenic-bound proteins in serum and haemoglobin. Arsenic in food products.
Cadmium Cd	Complex organic cadmium compounds, metallothionine.
Chromium Cr	Redox forms of chromium, Cr(VI) in the environmental. Chemical forms of chromium coupled with proteins.
Iodine I	Iodine forms in the environment and biological fluids.
Lead Pb	Forms of lead compounds in the environment, e.g. trialkylated Pb compound.
Phosphorus P	Phosphine (hydrogen phosphides) in indoor air at the workplace.
Mercury Hg	Forms of mercury compounds in the environmental and food products (in particular, methylmercurate).
Platinum Pt	Inorganic forms in the environment. Metallo-organic forms of cis-platinum in medicine (therapeutic).
Selenium Se	Inorganic and organometallic selenium compounds in the environment and food products.
Tin Sn	Organometallic forms in the environment and food products (e.g. shellfish).

Speciation analysis can be performed in at least five different types, depending on the aim and scope of the analytical investigation. Brief characteristics of basic types of speciation analysis and examples of their application are given in Table 2.3.

Table 2.3 Characteristics of basic types of speciation analysis [8]

Type	Application area	Remarks
-	Environmental pollution analysis. (air, water, soil).	*Physical speciation* This type of speciation analysis is extremely important from various point of view: chemical process investigations and biochemical processes going on in different elements of environment.
Screening speciation	Environmental pollution analysis. Food pollution analysis. Ecotoxicology.	*Chemical speciation* It is simplest case of speciation analysis, which leads to the detection and determination of one definite analyte.
Group speciation	Environmental pollution analysis. Food pollution analysis. Ecotoxicology.	This case of speciation analysis leads to the determination of the concentration level of the specific group of compounds or elements existing in different compounds and forms and at the specific oxidation level.
Distribution speciation	Environmental pollution analysis. Ecotoxicology.	This type of speciation is connected in most cases with the analysis of biological samples.
Individual speciation	Environmental pollution analysis. Food pollution analysis. Ecotoxicology.	The most difficult form of speciation analysis. Fractionation and separation techniques have played a particular role. Unique application of chromatography and coupled techniques in this area of speciation analysis.

2.4 Literature review: speciation of chromium

There is an increasing demand for information about speciation of chromium because their toxicity depends on the chemical form. As the total content of chromium in the environment does not generally exceed several $\mu g\ L^{-1}$, evaluation of chromium toxicity in environmental and biological samples requires a sufficiently sensitive method but its specificity is an important role regarding to speciation, e.g. oxidation state. There are a few analytical techniques available that have sufficient sensitivity and selectivity for the direct determination and speciation of trace levels of chromium in water. Sample pretreatments, which include analyte separation and preconcentration are required in order to determine the low levels of the individual chromium species, even when the most sensitive techniques such as electrothermal atomic absorption spectrometry (ETAAS), inductively coupled plasma atomic spectrometry (ICP-AS) and flame atomic absorption spectrometry (FAAS) are used [31].

The literature on the speciation of chromium using atomic spectrometric techniques has been classified into three groups, according to the different pretreatments employed: group I is complex formation, oxidation-reduction, extraction, group II is precipitation/co-precipitation, and group III is preconcentration on column.

- Complex formation, oxidation - reduction, extraction

Complex formation is one of the most widely applied techniques for speciation of chromium. Depending on its oxidation state chromium can form different complexes which can be determined by UV-Vis spectrophotometry, for example the spectrophotometric method of Cr(VI) determination with diphenylcarbohydrazide [32]. Another interesting work was a method of Cr(VI) determination, based on the fluorescence produced from the ion-association complex between the crystal violet cation and iodochromate anionic complex, in the presence of Cr(III) without pre-separation of the two

oxidation states [33]. Cr(III) and Cr(VI) species could also be determined directly using cathodic stripping voltametry with the collection of complex Cr(III)-diethylenetriamine-pentaacetic acid on mercury drop electrode [34].

Extraction processes are frequently used after complex formation to extract the complex from prior to their determination. A routine method, recommended by USEPA (method 218.4), consisted of the extraction of Cr(VI) with ammonium pyrrolidinecarbodithioate (APDCT) into methyl isobutyl ketone (MIBK), followed by the determination of chromium in MIBK using AAS method [35]. Total chromium was determined in the same way after oxidation of Cr(III) to Cr(VI). However, other organic solvent such as chloroform was often used but the determination of chromium was performed after back-extraction of Cr-APDCT complex with nitric acid solution for AAS.

- Precipitation / co-precipitation

One of precipitation methods often used was the method proposed by Nakayama et al. [36]. Cr(III) was recovered by Fe(III)-hydroxide and both Cr(III) and Cr(VI) were collected by Bi(I-II)-hydroxide. The co-precipitation with lead salt described by Obiols et al. [37] was developed to improve less time-consuming chromium speciation procedure.

- Preconcentration on column

The most frequently used pretreatment on AAS techniques is preconcentration on columns on which the retention and subsequent elution of one or two species are permitted. Two preconcentration strategies have been employed:

(1) Preconcentration of one species

Only one species (Cr(III) or Cr(VI)) is preconcentrated, while the other species is often complexed or measured directly.

Preconcentration of Cr(III) or Cr(VI) has been carried out using different types of sorbents. In some case, Cr(III) is oxidized to Cr(VI), total chromium is measured and the Cr(III) content is calculated by the difference. In some case, the reduction of Cr(VI) to

Cr(III) is carried out, total chromium is measured and the Cr(VI) content is calculated by the difference. Example of sorbents for chromium preconcentration are given in Table 2.4.

Table 2.4 Example of sorbents for preconcentration of one chromium species

Sorbents	Species	Experimental conditions	Ref.
Anion-exchange Bio-Rad 1-X4	Cr(VI)	-	[38]
Anion-exchange resin Sephadex DEAE A-25	Cr(VI)	-	[39]
Ambersorb 563 resin	Cr(VI)	oxidize Cr(III) to Cr(VI) by $K_2S_2O_8$ in acid medium.	[40-41]
Melamine based polymeric succinic acid resin	Cr(VI)	oxidize Cr(III) to Cr(VI) by H_2O_2 in basic medium.	[42]
Amberlite XAD-16 resin	Cr(VI)	oxidize Cr(III) to Cr(VI) by $KMnO_4$ in acid medium.	[43]
C-18 silica	Cr(VI)	oxidize Cr(III) to Cr(VI) by $KMnO_4$ in acid medium and require Cr(III)-DDTC complex for sorption.	[44]

Table 2.4 *(continue).*

Sorbents	Species	Experimental conditions	Ref.
Polar phase aromatic sulphonic acid silane	Cr(III)	-	[38]
Maleic acid –functionaliized XAD resin	Cr(III)	reduce Cr(VI) to Cr(III) by Na_2SO_3	[45]
Chromosorb 108	Cr(III)	reduce Cr(VI) to Cr(III) by conc. H_2SO_4 in ethanol and require Cr(III)-dithizone complex for sorption	[46]

(2) Preconcentration of both species

Both species are preconcentrated, either in the same column or in different columns. Retention of Cr(III) and Cr(VI) in the same sorbent can be carried out in different types of column packed with sorbents such as silica gel loaded with anion exchanger [47], activated alumina [48] and polymeric sorbent with aminocarboxylic groups [49]. Table 2.5 and Table 2.6 show the example of solid sorbents for retention of Cr(III) and Cr(VI) in the same sorbent and different sorbents, respectively.

Table 2.5 Example of sorbents for retention of Cr(III) and Cr(VI) in same sorbent

Sorbents	Remarks	Ref.
2-Naphthol-3,6 disulfonic acid functionlized resin	pH value for retention of Cr(VI) is 1.5 but Cr(III) can be retained at pH 6.5.	[5]
Baker's yeast cells immobilized on controlled pore glass	require sequential elution of chromium species from sorbent.	[13]
C_{18} bond silica gel	Cr(III) and Cr(VI) are complexed with DDTC at pH 4-9 and 1-2, respectively before sorption.	[44]

Table 2.6 Example of sorbents for retention of Cr(III) and Cr(VI) in different sorbents

Sorbents		Remarks	Ref.
Cr(III)	Cr(VI)		
Zirconium (IV) phosphate	Zirconium (IV)	pH value for retention of Cr(VI) is 3 but Cr(III) can be retained at pH 5.0-9.0.	[3]
731 cation exchange resin	717 anion exchange resin	Cr(III) and Cr(VI) can be retained at pH 6.0.	[50]
Chelex-100	Anion exchange (AG-MP-1)	Cr(III) and Cr(VI) can be retained at pH 4.5.	[23]
IDA-Novarose	Q-Sepharose	Cr(III) and Cr(VI) can be retained at pH 3.0.	[51]

From the literatures, the use of SPE in chromium speciation analysis was reported, but these works still had several steps in the sample pretreatment such as the adjusting pH of solution and the changing form of chromium, Cr(VI) to Cr(III) or Cr(III) to Cr(VI), which had some disadvantages due to incompleteness in oxidation and reduction. In addition, preconcentration normally involved extra manipulations of the sample and additional reagents resulting in bad effect on sample contamination and/or loss of sample. Therefore, these problems should be minimized.

Silica gel immobilized with various organic compounds as metal chelating agent has received great attention, due to a large number of the reactive sites of silica gel, and therefore the number of organic molecules immobilized is high which results in good sorption capacity for trace elements [52].

From previous publications, amidoxime and benzothiazolyl groups have been known for their capabilities of chaleting agent. As(III) extraction using amidoxime functionalized on polymer was reported [53]. The reactive fiber containing amidoxime group provided high selectivity to Au(III) [54], and uranium was also extracted by amidoxime fiber [55].

For benzothiazolyl group, it is well known that the nitrogen in benzothiazolyl group can act as a donor atom for transition metal ions. 2-Mercaptobenzothiazole has been suggested as a chelating agent for Bi(III), Cd(II), Co(II), Cu(II), Au(III), Pb(II), Hg(II), Ni(II), Tl(III) and Zn(II) [56]. 2-(*o*-hydroxyphenyl)-benzothiazole gives precipitate with Cu(II), Cd(II), Pb(II), Co(II) and Ni(II) in acetic-acetate buffer [57]. *N*-benzothiazol-2-yl-benzamide formed complexes with Cu(II), Ni(II), Pd(II) and Zn(II) upon deprotonation [58].

From the consideration above, the amidoxime and benzothiazolyl groups were chosen as a functional group to modify on surface of silica gel. These modified silica gels were applied to use as solid sorbent for chromium speciation.