

Extractant Impregnated Membranes for Chromium(III) and Chromium(VI)

by

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Abstract

An innovative sampling technique employing extractant impregnated membranes is presented for the selective sorption and stabilization of specific oxidation states of chromium. Polymer-based selective ion traps employing the extractants tricaprylmethylammonium chloride (*Aliquat-336*) and di-(2-ethylhexyl) phosphoric acid (*DEHPA*) were used for the selective removal and enrichment of the anionic forms of Cr(VI) and cationic forms of Cr(III), respectively. Results show Aliquat-336 and DEHPA effectively remove Cr(VI) and Cr(III) from aqueous solutions. Extraction efficiency is independent of source concentration from 1 <x> 50 ppm but is dependent upon time, pH of the source, ionic strength, extractant concentration, composition of source phase, and choice of stripping agent and stripping agent concentration. Optimum conditions for Cr(VI) and Cr(III) were determined to be 1 v/v% Aliquat-336 and 30 v/v% DEHPA; an extraction time of at least 3-5 days; source phase pH between 3-5; and 1 M NaOH/ 0.5 M HNO₃ as stripping agent for Cr(VI) and Cr(III) species, respectively. Batch extraction efficiencies of 97 +/- 3 % were obtained for the optimal conditions. Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) was used for total chromium determination. UV-VIS spectrometry was used for Cr(VI) determination. Scanning Electron Microscopy revealed the physical structure of the polymeric supports and subsequent impregnation was evidenced by the SEM images. X-ray photoelectron spectroscopic results provided the elemental composition of the Versapor[®]-450 membrane to be 71.5% C, 7.0% O, 9.5% Cl and 12.0% N. The Whatman[®] PP membrane was 100.0 % C. Elemental composition of 1 v/v% Aliquat-336 on Versapor[®]-450 and Whatman[®] PP membrane was 92.3% C, 0.8% O, 3.6% N, and 3.3% Cl and 94.3% C, 3.3% N, and 2.4% Cl, respectively. Elemental composition of 30 v/v% DEHPA on Versapor[®]-450 and Whatman[®] PP membranes were 78.8% C, 3.4% P, 17.8% O and 76.3% C, 19.3% O, 4.4% P, respectively. Column studies under simulated groundwater conditions utilizing the extractant impregnated membranes showed no statistical difference in Cr(VI) recoveries from those obtained in batch experiments. Cr(III) extraction revealed a statistical difference in analyte recovery vs. batch experiments. This is attributed to the lowered pH and cationic interferences present in simulated groundwater.

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Chapter 1

1. Introduction

During the last two decades, an increased interest has arisen toward the study of heavy metals in environmental systems. Of particular interest are the environmental fate, sampling, and speciation of metals. Many heavy metals enter the environment by several natural processes and an even larger portion enters the environment through human activities [1]. Chromium is an example of an important heavy metal that is used in the manufacture of many diverse products. Chromium in the environment is ubiquitous and the impact of its presence far-reaching. Chromium to the environment originates from both natural and anthropogenic sources [2]. Chromium compounds are highly varied and widely distributed in the occupational, domestic, and recreational environments. The interest in chromium (Cr) speciation originates from widespread use of this metal in various industries such as metallurgical (steel, ferro- and nonferrous alloys), refractories (chrome and chrome-magnesite), and chemical (pigments, electroplating, tanning, other) [3]. Chromium, while not unique in properties, is commonly used in various industries because of its metallic characteristics.

Inadequate disposal of hazardous wastes containing chromium are often the major anthropogenic source of chromium to the environment. The environmental chemistry of chromium is quite complex. Once chromium enters in the environment, the element may undergo many processes. The chemistry of chromium compounds in environmental matrices involves oxidation-reduction transformations, precipitation-solubilization reactions, and adsorption-desorption phenomena. Chromium speciation is primarily dependent upon pH and redox conditions. Oxidation and reduction reactions can convert Cr(III) to Cr(VI) and vice versa. The relationship between Cr(III) and Cr(VI) depends on a balance between oxidation and reduction. The pH is the master variable that controls the balance between the two opposing reactions.

Many inorganic compounds are necessary in plant and animal nutrition while others may be toxic to living matter. Inorganic environmental contaminants are particularly problematic because unlike most organic contaminants they do not undergo

degradation [1]. Redox reactive metals often have different degrees of toxicity depending on the specific metal oxidation state. Chromium is one such metal ion that persists in the environment as either Cr(III) or Cr(VI) and depending upon its oxidation state; may be considered toxic or essential to living organisms. Hexavalent chromium is 10-100x's more toxic than trivalent chromium. While Cr(III) is an essential element for living beings, playing an important role in carbohydrate metabolism, Cr(VI) becomes carcinogenic after long exposures. Hence, Cr(VI) incurs a significant health risk to human health when released into the environment. Cr(VI) poses a greater health risk due to its high solubility in water and consequential mobility. Trivalent chromium, on the other hand, is relatively innocuous and under ambient environmental conditions Cr(III) is insoluble in water and immobile. The mobility and toxicity of chromium depends on its oxidation state, therefore speciation of Cr is important in determining its fate and location in the environment.

The complex chemistry of chromium in the environment lies within the various speciation states of the metal ion. The fate, speciation and transport of chromium in groundwater have gained great attention in scientific literature in recent years. The drastic contrast in physiological behavior between Cr(III) and Cr(VI) has become the reason it is critical to differentiate between both oxidation states when analyzing environmental samples. Not only is the total metal concentration of interest, but also it is now accepted that understanding the environmental behavior by determining its speciation is of paramount importance. Most of the work has focused on evaluating the extent of chromium contamination and the processes that affect its mobility and retardation in groundwater. Another portion of literature deals with the development of analytical methodologies, which can be used in the total determination of chromium. An even smaller fraction of literature focuses on the determination of specific speciation states of chromium.

The sampling of contaminated groundwater at hazardous waste sites continues to be an extremely costly endeavor, the effectiveness of which is often uncertain at best. Oxidation of Cr(III) to Cr(VI) and reduction of Cr(VI) to Cr(III) can occur

simultaneously in the environment. Interconversion and degradation processes encompassing chromium chemistry make sampling difficult. Often, laboratory measurements do not reflect the concentrations of species taken at the point of collection. Elements such as chromium dominate speciation studies in the search for sampling methods, which can preserve and stabilize individual fractions upon sample collection. New, *in-situ* technologies must be developed that are capable of the separation and the preservation/stabilization of each fraction.

Despite the significant advances that have been made in metal speciation analysis techniques over the past 25 years, much remains to be done. Published papers on Cr speciation generally demonstrate high sensitivity and selectivity but there is an urgent need for reproducible sampling and minimal sample preparation, good separation, and metal species preservation [4]. The lack of analytical procedures for sample storage and individual species preservation precludes the development of routinely acceptable speciation methods. To minimize perturbation of the systems like anoxic waters, the sediment-water interface and colloidal materials, some new analytical methods for Cr species determination *in-situ* have to be developed.

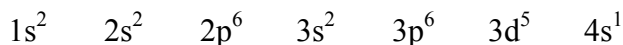
It is the purpose of this work to present a literature summary on the physical and chemical properties of chromium, sources of chromium to the environment, chemistry of chromium in soil, water, and air, physiology and toxicology effects of Cr, environmental fate, distribution and transport of chromium, and the chemical transformations of chromium in water. Additionally, an innovative sampling technique employing extractant impregnated membranes will be presented in which the sampling, preservation and stabilization of chromium species is accomplished. The potential impacts of this project on advancing knowledge in the area of science are far-reaching. This work presents the process of how sampling and storage should be handled to obtain accurate results in regards to chromium speciation, which is an area of little study. Additionally, the technique presented allows an accurate representation of the sample taken at the point of collection, which is often a problem plaguing chromium sampling and storage. As a result, hazards of chromium-bearing wastes will be accurately evaluated. This study

avoids problems associated with stabilization and preservation of individual fractions of chromium species in solution. In contrast to existing methods that have severe stability, economic, and technical problems.

1.1 Physical and Chemical Properties of Chromium

Chromium, atomic number 24, is located in group VIA of the periodic table and is a member of the first transition series. Chromium is a steel-gray, lustrous metal that melts at 1903 +/- 10°C [4]. It has a body centered crystalline structure and is as hard as corundum and less fusible than platinum [5]. It dissolves easily in mineral acids that are non-oxidizing. It does not dissolve in nitric acid (concentrated or dilute) or cold aqua regia probably due to passivation; thus the use of the metal as a protective corrosion inhibitor, *viz.*, chromium plating and metal finishing formulations [4].

The inorganic chemistry of chromium is important to the aqueous chemistry of the metal. Chromium is rich not only rich in its variety of colors, but also in its many oxidation states and the geometries of its many compounds as shown in Table 1 [4]. Cr can exist in several chemical forms displaying oxidation numbers from -2 to +6, but it most commonly occurs as Cr(VI) and Cr(III) [6]. Cr(VI) and Cr(III) are the speciation states of interest in this work. The Cr(V) and Cr(IV) are important intermediates states that influence the rate of reduction of the hexavalent state. Cr(VI) does not always convert directly to Cr(III), but may be initially reduced to Cr(V) or Cr(IV) [7]. The chemical and physical properties of chromium are summarized in Table 2 [5]. The ground state electron configuration of the chromium atom is [2]:



while for the most prevalent states, Cr⁺³ and Cr⁺⁶, it is 3d³ 4s⁰ and 3d⁰ 4s⁰, respectively [4]. These two ground states exist mainly in the octahedral (⁴A_{2g}) and tetrahedral (¹A₁) geometries respectively [4]. Other geometries and oxidation states are listed in Table 3.

Table 1. Chromium (III) Compounds.

OXIDATION STATE +3								
chromic chloride	chromium chloride (CrCl_3); chromium (III) chloride; chromium trichloride	CrCl_3	bright purple plates	hexagonal, D_3^3 or D_3^5	2.87_{2s}	subl	885	insol H_2O , sol presen Cr^{2+}
chromic acetylacetonate		$\text{Cr}(\text{CH}_3\text{COCHC}(\text{OCH}_3)_3)_3$	red-violet crystals	monoclinic	1.34	208	345	insol H_2O ; sol C_6H_6
chromic potassium sulphate (chromic alum)	chromic alum (dodecahydrate); chromic potassium sulphate; potassium chromium sulphate; potassium chromium alum; potassium chromium sulphate; potassium disulphatochromate (III).	$\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	deep purple crystals	cubic, A_n^6	1.826_{1s}	89 (incongruent)		sol H_2O
chromic chloride hexahydrate	0% Basicity chromic alum; Crystal chromic alum.	$(\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2)\text{Cl} \cdot 2\text{H}_2\text{O}$	bright green crystals	triclinic or monoclinic	1.835_{2s}	95		sol H_2O , green soln turning green-violet
OXIDATION STATE +3								
chromic chloride hexahydrate		$(\text{Cr}(\text{H}_2\text{O})_6)\text{Cl}_3$	violet crystals	rhombohedral, D_3^6 d		90		sol H_2O , violet soln turning green-violet

Table 1 (cont'd). Chromium (VI) Compounds.

OXIDATION STATE +6						
chromium (VI) oxide	CrO_3	ruby-red crystals	orthorhombic, C_{16}^{20}	2.7 ₂₅	197	dec
chromyl chloride	CrO_2Cl_2	cherry-red liquid		1.9145 ₂₅	-96.5	115.8
ammonium dichromate	$(\text{NH}_4)_2\text{Cr}_2\text{O}_7$	red-orange crystals	monoclinic	2.155 ₂₅	dec. 180	v sol H_2O ; sol CH_3COOH , $(\text{CH}_3\text{CO})_2\text{O}$ insol H_2O , hydrolyzes; sol CS_2 , CCl_4 , sol H_2O
potassium dichromate	$\text{K}_2\text{Cr}_2\text{O}_7$	orange-red crystals	triclinic	2.676 ₂₅	398	dec sol H_2O
	Chronic acid ($\text{H}_2\text{Cr}_2\text{O}_7$), dipotassium salt; dichromic acid dipotassium salt; dipotassium dichromate; lopezite; potassium bichromate; potassium dichromate (VI)					
sodium dichromate	Bichromate of soda; chromic acid ($\text{H}_2\text{Cr}_2\text{O}_7$), disodium salt; chromium sodium oxide; disodium dichromate; dichromic acid, disodium salt; sodium bichromate; sodium chromate; sodium dichromate (VI).	$\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ orange-red crystals	monoclinic	2.348 ₂₅	84.6 incon- gruent	dec v sol H_2O

Property	Value
Atomic Weight	51.996
Atomic Number	24
Density (g/ml)	7.14
Melting Point	1900°C
Boiling Point	2642°C
Heat Capacity	5.58 cal/g-atom (25°C)
Latent Heat of Fusion	3.5 kcal/g-atom
Latent Heat of Vaporization	81.7 kcal/g-atom

Table 2. Physical and Chemical Properties of Chromium.

The Latimer diagrams for acid and base solutions are illustrated in Figure 1. The diagrams show that in aqueous solution the +3 state is the most stable, followed by the +2 state [4]. Considerable energy would be required to convert Cr(III) to higher or lower states [3]. The negative standard potential (E°) of the Cr(III)/Cr(II) metal ion couple signifies that Cr(II) is readily oxidized to Cr(III), and Cr(II) species are stable only in the absence of any oxidant (anaerobic conditions) [3] (Figure 2). The +6 state is unstable in acid solution and goes to the +3 state. Cr(VI) in acidic solution demonstrates a very high positive redox potential (E° within 1.33 to 1.38V) which denotes that it is strongly oxidizing and unstable in the presence of electron donors. Furthermore, chromium in the +2 state is a good reducing agent, while in the +6 state it is a powerful oxidizing agent [4].

Divalent chromium is relatively unstable, being rapidly oxidized to the trivalent form. Thus, only two forms of chromium species, the trivalent and hexavalent Cr, are stable enough to occur in the environment. Cr(III) and Cr(VI) are drastically different in charge, physicochemical properties as well as chemical and biochemical reactivity [3]. The complex chemistry of chromium has been the focus of many studies due to the difficulty in determining the speciation of chromium in environmental matrices. This attention is due to the oxidation states of chromium, which affects human toxicity and ecotoxicology as well as the physiochemical processes of mobility and transport in groundwater. The essentiality or carcinogenicity of chromium is a function of its chemical form [2]. Oxidation state and solubility are particularly important to the biological effects of chromium compounds [2].

1.2 Natural Sources of Chromium

Elemental chromium is not found in nature. The most important naturally occurring chromium mineral is chromite, FeCr_2O_4 , with Cr(III) on octahedral sites and Fe(II) on tetrahedral sites, [8]. Cr(III) is also found in a number other minerals. Chromium may exist naturally in the (VI) oxidation state, but is less stable in

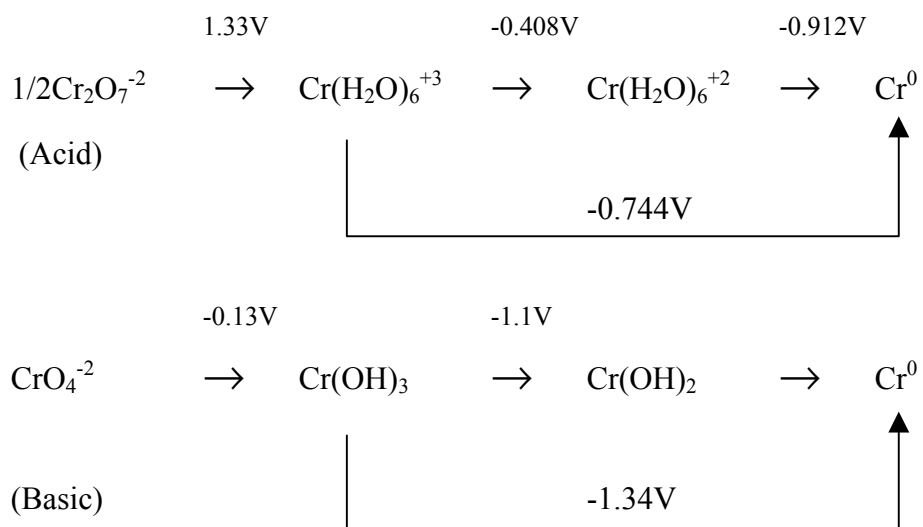


Figure 1. Latimer Diagrams for Acid and Base Solutions. Reproduced with permission from *Environmental Health Perspectives* [4].

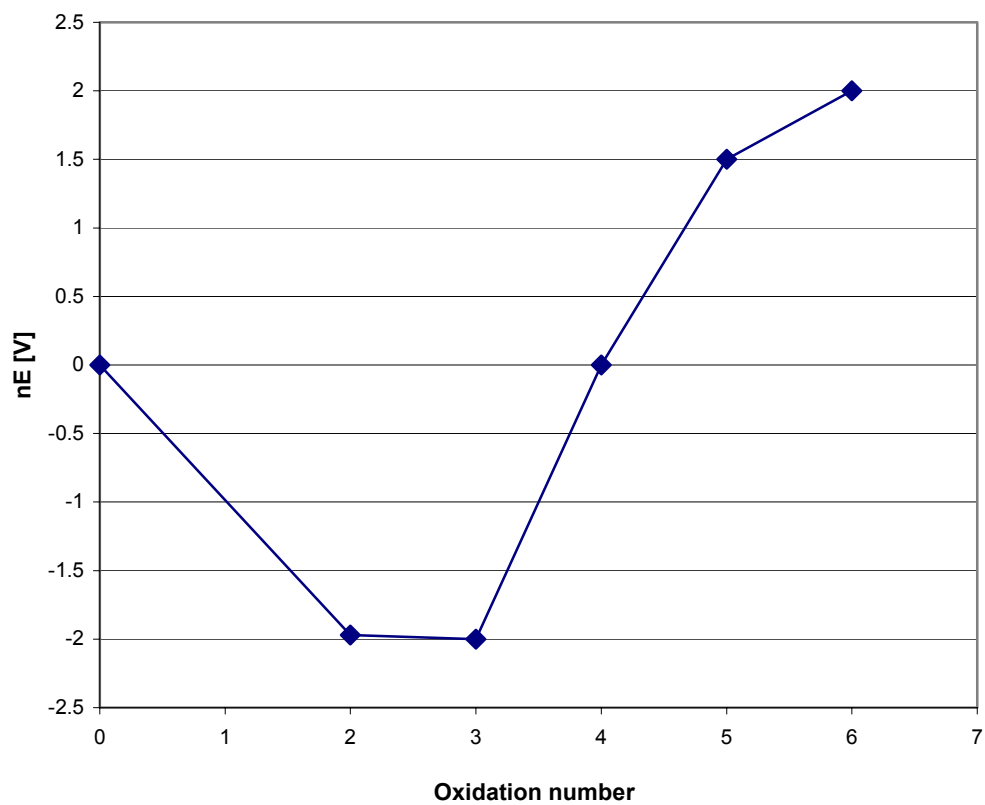


Figure 2. Frost Diagram for Chromium Species in Acidic Solution.

Compound	Geometry	Oxidation State
$[\text{Cr}(\text{CO})_5]^{-2}$	Trigonal bipyramid	-2
$[\text{Cr}(\text{CO})_{10}]^{-2}$	Octahedron	-1
$[\text{Cr}(\text{bipy})_3]$	Octahedron	0
$[\text{Cr}(\text{CNR})_6]^+$	Octahedron	+1
$[\text{Cr}(\text{CO})_2(\text{diars})_2\text{X}]^+$	Capped trigonal prism	+2
$[\text{Cr}(\text{Cl})_4]^{-1}$	Tetrahedron	+3
$[\text{CrF}_6]^{-2}$	Octahedron	+4
$[\text{CrOCl}_4]^{-1}$	Square pyramid	+5
$[\text{CrO}_4]^{-2}$	Tetrahedron	+6

Table 3. Representative Formal Oxidation States and Properties of Chromium.
Reproduced with permission from *Environmental Health Perspectives* [4].

reducing environments [8]. Cr is commonly found in rocks, soils, plants, animals, and in volcanic dust and gases. Elemental chromium was first prepared and characterized by Louis Vauquelin in 1797 [2]. Its name reflects the many colors of its compounds as was shown in Table 1. In the earth's crust, chromium ranks fourth in abundance among the 29 elements of biological importance from both the essential and toxic perspectives [2]. Chromium is more abundant than cadmium, cobalt, copper, lead, molybdenum, nickel or zinc. Weathering is responsible for the natural concentrations of chromium in underground and surface waters, soils, "continental dust", and air [2]. The average concentration of chromium is 100 mg/kg [2]. Natural contributions to the total concentrations of chromium in the environment are complemented by somewhat (~50%) larger quantities of chromium released by human activities.

1.3 Anthropogenic Sources of chromium

From an economical point of view, the advantages of chromium applications in such a wide range of industries, contrast with its negative external effects as a hazardous pollutant [9]. Chromium is and has been ubiquitous [2]. Due to industry processes, large quantities of Cr compounds are discharged as liquid, solid, and gaseous wastes into the environment and can ultimately have significant and adverse biological and ecological effects [3]. Chromium is often released into the environment through the manufacturing, inadequate disposal of products or chemicals containing chromium, or the burning of fossil fuels that release chromium to the air, soil, and water.

1.3.1 Metallurgy

Approximately 57% of imported chromite ore is used in the metallurgic industry [6]. The metallurgic industry uses ores containing at least 50% chromic oxide for ferrochrome, which is used primarily in stainless steels. The chromium used in the metallurgic industry is mainly trivalent, or in the zero oxidation state. Metallurgic-grade chromite ore is usually converted into one of several types of ferrochromium or chromium metal that are alloyed with iron or other elements (usually nickel or cobalt [6]. These are then used in making various steels (60% stainless steel, the remainder is used in high-speed steels, alloy steels, high temperature steels, and nonferrous alloys) [6].

Most of the chromium released to the environment from these operations will be elemental or trivalent chromium. These forms will have little impact on the environment [8].

1.3.2 Chemical Industries

The chemical industry uses ore containing approximately 45% chromic oxide for the preparation of sodium chromate and sodium dichromate, from which most other chromium chemicals are produced [6]. Chromates are manufactured from chromite ore and are the primary product from which other compounds are manufactured [8]. Trivalent chromium dusts are emitted during initial stages of the conversion of ore to chromate and chromate dusts are emitted after oxidation of the ore [8]. There will be chromium entering the environment from many industries that use chromates or dichromate as a raw material. Some of these include: catalyst, paint, pigment, textile, graphic arts, fungicide, corrosion inhibitor, paper match, fireworks, and dry cell batteries industries [8]. A majority of chromic acid produced is used in chrome plating. This process results in chromic acid aerosols released by bubbles of hydrogen in the solution, which are exhausted to air [6]. It has been found that industrial workers dealing with the industries listed above have been exposed to hexavalent chromium [6].

1.3.3 Refractory Industry

The refractory industry uses ores containing approximately 34% chromic oxide and high alumina content for melting-furnace linings, because chromite has a high melting point (2040°C) and is chemically inert [6]. In addition to their use as chromite bricks or magnesia-chrome bricks, chrome refractory materials may be used as coatings to close pores and for joining bricks within the furnace [6]. The use of chromite is important but declining, as open hearths are replaced by basic-oxygen furnaces. The chromium used in the refractory industry is trivalent chromium in the form of chromite ore.

1.3.4 Coal

The chromium contents of fossil fuels are low, but combustion of large quantities of coal (containing 5-50 ppm Cr) and of oil (containing 0.1-1 pm Cr) are the major anthropogenic source of environmental chromium in the United States. Of the total anthropogenic airborne chromium emissions in the United States, approximately half result from fossil fuel combustion [2]. The ashes from the combustion of fossil fuels, which contain significant amounts of chromium, are disposed of by landfilling. Emissions from chromium chemical manufacturing facilities, from many cooling towers, and from steel mills are other major sources of airborne chromium. Recent EPA estimates of anthropogenic chromium airborne emissions in the USA are listed in Table 4 [2]. Approximately one-third of the more recently reported total is expected to be in the toxic form.

Numerous soils, waste sites, groundwaters, and surface waters are contaminated with anthropogenic Cr [9]. Industrial and domestic wastes are also dispatched to landfills for disposal. Sewage sludge compost piles and steel mill slag heaps are additional wastes to be considered as potential sources of chromium for the contamination of soil and groundwater. Chromium concentrations in some of these wastes are tabulated in Table 5 [2]. Patrick *et. al.* have reviewed the relationships among groundwater quality and quantity, surface water, and land use. These relationships must be taken into consideration in developing groundwater protection and management strategies [2]. The potential for surface water contamination is greater than that for groundwater contamination. Metal finishing and leather tanning activities contribute significant amounts of chromium to surface waters by way of their discharges to municipal sewage collection systems [2]. These wastes are also among the more significant anthropogenic point source discharges of chromium to surface waters.

Source Category	Cr Emitted per year (tons)	Speciation
Coal and oil combustion	1723	99% Cr(III)
Chemical manufacturing	473	100% Cr(VI)
Steel production	103	98% Cr(III)
Primary metal production	72	100% Cr(VI)
Ferrochromium production	16	95% Cr(III)
Petrochemical cooling towers	197	100% Cr(VI)
Comfort cooling towers	7-200	100% Cr(VI)
Tobacco industry cooling towers	5	100% Cr(VI)
Utility industry cooling towers	5	100% Cr(VI)
Tire/ rubber industry cooling towers	4	100% Cr(VI)
Glass industry cooling towers	3	100% Cr(VI)
Chrome plating industry	56	100% Cr(VI)
Textile manufacturing industry	35	100% Cr(VI)
Refractories production	24	99% Cr(III)
Sewage sludge incineration	13	99% Cr(III)
Municipal sludge waste incineration	2.5	99% Cr(III)
Cement production	3	99% Cr(III)
Chrome ore refining	4.8	99% Cr(III)

Table 4. U.S. EPA estimates of atmospheric chromium emissions from anthropogenic sources in the US.

Waste	Chromium Content (ppm)
Electroplating sludge	11,555
Electroplating sludge	130,000
Steel mill pickle liquor	2,300
Steel mill slag	100-200
Steel mill slag	9,000-48,000
Coal fly ash	196
Coal fly ash	250
Coal fly ash	172
Sewage sludge	50-13,349
Incinerator fly ash	1,250-1,600
Incinerator fly ash	400
Incinerator fly ash	77
Incinerator bottom ash	270
Incinerator bottom ash	149

Table 5. Chromium Concentrations in Some Wastes Disposed of on/in Soil.

Chromium is now known to contaminate 33% of the hazardous waste sites on EPA's National Priorities List (NPL) at a maximum containment level (MCL) of 0.1ppm [10]. Upon entry into a soil system, the fate and potential bioavailability of Cr depends on the chemical form of chromium and the chemical and mineralogical properties of the soil environment. In general, toxic Cr released into soil low in organic matter and Fe and Al oxides favors high Cr mobility.

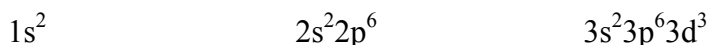
1.4 Chromium (III)

The contrast in behavior between Cr(III) and Cr(VI) has become the reason it is critical to differentiate between both oxidation states when analyzing environmental samples. Thermodynamically, Cr (III) is the most stable oxidation state and occurs naturally in the environment. It is represented by thousands of compounds [4]. In this state, the chrome is labile and kinetically very slow to react or form complexes. Chromium (III) is also an essential nutrient in our diet, but needed in very small amounts. Cr(III) is considered to be a trace element essential for the proper functioning of living organisms. It is reported to be responsible for the control of glucose and lipid metabolism in mammals [3]. The required amount has been reported to be from 50 to 200 µg per day [4]. Cr(III) is not a strong oxidant and the human's natural body acidity is enough for the chrome to be kept in the Cr (III) state. Cr(III) also shares the quality with all other metals of being toxic to biological systems at some level. Fortunately its relative toxicity is low. This is due to the slow ligand exchange kinetics of Cr(III), causing it to be fairly unreactive. Although Cr(III) is not a significant hazard itself, the potential for Cr(III) oxidation to Cr(VI) can make its risk tantamount to that of the hexavalent form [11].

Wherever Cr(III) is found in nature, it will be found in close association with Al(III) and Fe(III), mainly because of the overwhelming prevalence of the latter two elements in the earth's crust [12]. The atomic radii of chromium, aluminum, and iron

(64, 67, and 54 pm, respectively) and, therefore, the ionic potentials of the trivalent ions are close enough that substitution of one for another occurs in many mineral and organic structures. In spite of the greater ionic potential of Al(III), Cr(III) and Fe(III) are stronger Lewis acids because of their need to share electrons in order to acquire the noble gas (krypton) configuration, whereas aluminum has only to lose three electrons to acquire the stable neon core [12]. Chromium (III) forms a multitude of complexes, both organic and inorganic, in a variety of colors. However, it is slower in forming them compared with aluminum. The result is stronger bonding, and hence chromium has replaced its aluminum analog for the tanning of leather. In spite of similarities, Al(III) and Cr(III) are fundamentally different. Chromium (III) has three unpaired electrons, and in giving up these electrons, Cr(III) becomes Cr(VI). Al(III) having none to give, does not oxidize [12].

The major chemical properties of trivalent chromium compounds in aqueous solution are characterized by the stability of the violet hexaaquachromium(III) ion, $\text{Cr}(\text{H}_2\text{O})_6^{3+}$, and the tendency to precipitate as polymers formed through oxo- and/or hydroxo bridging [2]. The most stable ion state of chromium is Cr(III). The electron configuration of trivalent chromium is:

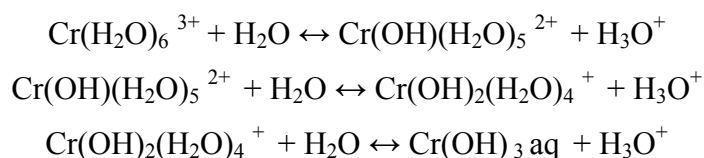


In aqueous solution, the hexaaquochromium (III) ion, $\text{Cr}(\text{H}_2\text{O})_6^{3+}$, demonstrates the octahedral geometry of d^2sp^3 hybridization and the kinetic inertness toward ligand exchange of the t^3_{2g} state with half filled shell stability [2]. This configuration is paramagnetic and not subject to field splitting [8].

Cr(III) is a hard acid which exhibits a strong tendency to form hexacoordinate octahedral complexes with a variety of ligands such as water, ammonia, urea, ethylenediamine, and other organic ligands containing nitrogen, oxygen, or sulfur donor atoms [13]. Cr(III) can also be chelated by organic molecules that are adsorbed to mineral surfaces [14]. Chromium (III) accepts electron pairs from many ligands to form a wide variety of coordination complexes, which may be cationic, neutral, or anionic, and essentially all of them are hexacoordinated [2]. Once formed, complexes of trivalent

chromium are quite stable. Ligand displacement, substitution, or exchange reactions are slow. Kinetically, these compounds are inert in keeping with the half-filled t_{2g} level of the d^3 configuration in octahedral geometry [4]. The violet hexaaquo species is inert to water exchange, $k = 3.5 \times 10^{-6} \text{ sec}^{-1}$ *i.e.* a half-life of a few days. Half times of tens of hours are not uncommon [2]. The complexation of Cr(III) by ligands other than OH^- increases its solubility when the ligands are in forms of discrete molecules or ions. When, however, donor atoms are bound in a macromolecular system, such as humic acids, then the Cr(III) complex is more or less immobile. If the complexation from these ligands can be neglected, under redox and pH conditions normally found in natural systems, Cr is removed from solution as $\text{Cr}(\text{OH})_3$ or in the presence of Fe(III), in the form of $[\text{Cr}_x\text{Fe}_{1-x}(\text{OH})_3]$ where x is the mole fraction of Cr [13].

The presence of Cr(III), concentration and forms in a given compartment of the environment depend on different chemical and physical processes, such as hydrolysis, complexation, redox reactions, and adsorption. In the absence of complexing agents, other than H_2O or OH^- , Cr(III) exists as the hexaqua ion $[\text{M}(\text{H}_2\text{O})_6]^{3+}$ and its hydrolysis products as shown below [2].



$\text{Cr}(\text{H}_2\text{O})_6^{3+}$ is a moderately strong acid ($\text{pK} \sim 4$) and deprotonated forms formulated shortly as $\text{Cr}(\text{OH})(\text{H}_2\text{O})_5^{2+}$, $\text{Cr}(\text{OH})_2(\text{H}_2\text{O})_4^+$, and $\text{Cr}(\text{OH})_3\text{aq}$ dominate successively within pH 4-10. As the pH of the system is raised, the hexaaquochromium (III) ion is neutralized to species such as $[\text{Cr}(\text{OH})(\text{H}_2\text{O})_5]^{2+}$ and $[\text{Cr}(\text{OH})_2(\text{H}_2\text{O})_4]^+$. These species polymerize through oxo- and hydroxo bridging [2].

The solubility of trivalent chromium compounds is limited by the formation of several oxide and hydroxide species [2]. The uncomplexed trivalent species is the chromic ion, Cr^{3+} , which is soluble in acidic solutions. Trihydroxochromium is however, sparingly soluble within pH range of 5.5-12 (minimum between pH 6.5 and 11.5) and overlaps considerably into the pH range of natural waters. In consequence, the hydroxo

complexes $\text{Cr}(\text{OH})(\text{H}_2\text{O})_5^{2+}$ and $\text{Cr}(\text{OH})_3_{\text{aq}}$ are expected to be dominant forms of Cr(III) in the environment [13]. Due to the fact that Cr(III) has limited solubility in the groundwater system, it is typically immobilized in the matrix. The formation of metal hydroxides plays an important role in the chemistry of chromium in soils and water systems. Cr(III) co-precipitates with many metal hydroxides [8]. In alkaline solutions, Cr(III) is either hydrolyzed or co-precipitates as $\text{Cr}(\text{OH})_3$ or $\text{Fe}_x\text{Cr}_{1-x}(\text{OH})_3$ [2]. In the pH range of 5-12, polynuclear species may also result from the formation of oxide or hydroxide bridges between trivalent chromium atoms. These polynuclear species condense to polymers, which initially precipitate as chromium(III) hydroxide [2]. Upon heating, or with time, or by raising the pH, the hexaquo species will hydrolyze to form polymers containing OH bridges as illustrated in Figure 3.

1.5 Chromium (VI)

In contrast, chromium (VI) is considered to pose the greatest human health risk because it is more toxic, more mobile, and more soluble in water than Cr(III) [7]. It serves no useful biological purpose to living things. Cr(VI) has been found to be acutely toxic, carcinogenic, and teratogenic [2]. Concentrations as low as 0.5 ppm in solution and 5 ppm in soils can be toxic to plants [11]. Cr (VI) is not a very stable state when compared to Cr (III). Cr (VI) is a very strong oxidising agent and therefore very fast in reacting, and subsequently harmful in biological systems. This fact warrants its regulation in the environment. The oxidizing power of Cr (VI) is a function of pH. As the pH becomes lower, Cr (VI) is more inclined to oxidize something. Fortunately, environmental samples are typically alkaline, and because the reduction potential of Cr (VI) decreases as pH increases, Cr (VI) is less reactive at these higher pH's [6].

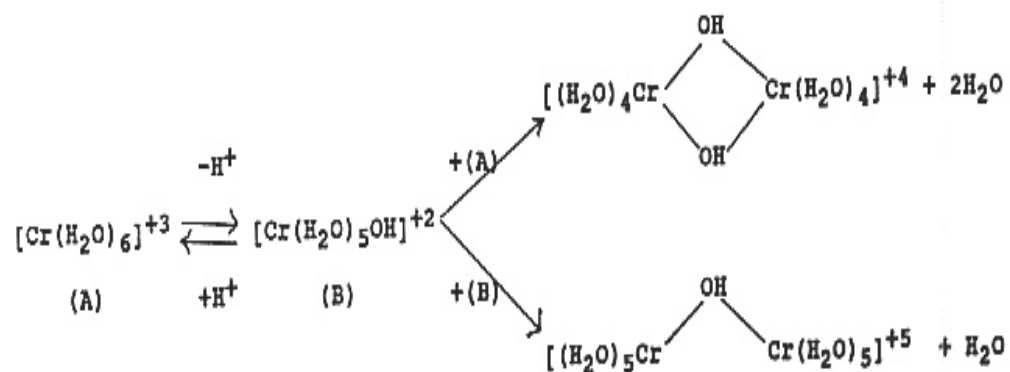


Figure 3. Polymeric Cr(III) species. Reproduced with permission from *Environmental Health Perspectives* [4].

The toxicological impact of chromates arises from the possibility of free diffusion across cell membranes [3]. The toxic properties of chromates of Cr(VI) originates from the action as an oxidizing agent , as well as from the formation of free radicals during the reduction of Cr(VI) to Cr(III) occurring inside the cell [3]. Cr(III) formed there in a significant concentration can cause further adverse effects because of its high capability to coordinate various organic compounds, which results in inhibition of the metallo-enzyme system [3]. Occupational exposure to hexavalent Cr compounds leads to a variety of clinical problems. Inhalation and retention of Cr(VI)-containing materials can cause perforation of the nasal septum, asthma, bronchitis, pneumonitis, inflammation of the larynx and liver, and increased incidence of bronchogenic carcinoma [3]. Skin contact of Cr(VI) compounds can induce skin allergies, dermatitis, dermal necrosis, and dermal corrosion [13].

Cr(VI) exhibits high solubility and mobility in groundwater because it forms anionic species. Since under alkaline to slightly acidic conditions hexavalent compounds are not strongly absorbed by many soils, thus they are very mobile in surface environments [15]. The hexavalent species exists primarily as chromic acid (H_2CrO_4) and its salts, hydrogen chromate ion (HCrO_4^-) and chromate ion (CrO_4^{2-}), depending on pH. The predominant species present, as a function of pH, are H_2CrO_4 at pH's less than 1, HCrO_4^- at pHs between 1 and 6, and CrO_4^{2-} at pH's above 6 (Figure 4). [16] The dichromate ion ($\text{Cr}_2\text{O}_7^{2-}$) is a dimer of HCrO_4^- , less a water molecule, which forms when the concentration of chromium exceeds approximately 1g/L [16]. At low pH, the anionic hexavalent species of chromium compounds are strongly adsorbed by mineral solids having exposed hydroxyl groups on their surfaces.

Hexavalent chromium may exist in the aqueous phase in different forms; the total amount of chromium and the pH are the main variables of the chromium (VI) species in an aqueous phase [17]. If there are no other chemical species in the aqueous solution, the Cr(VI) equilibrium reactions are [17,18]:

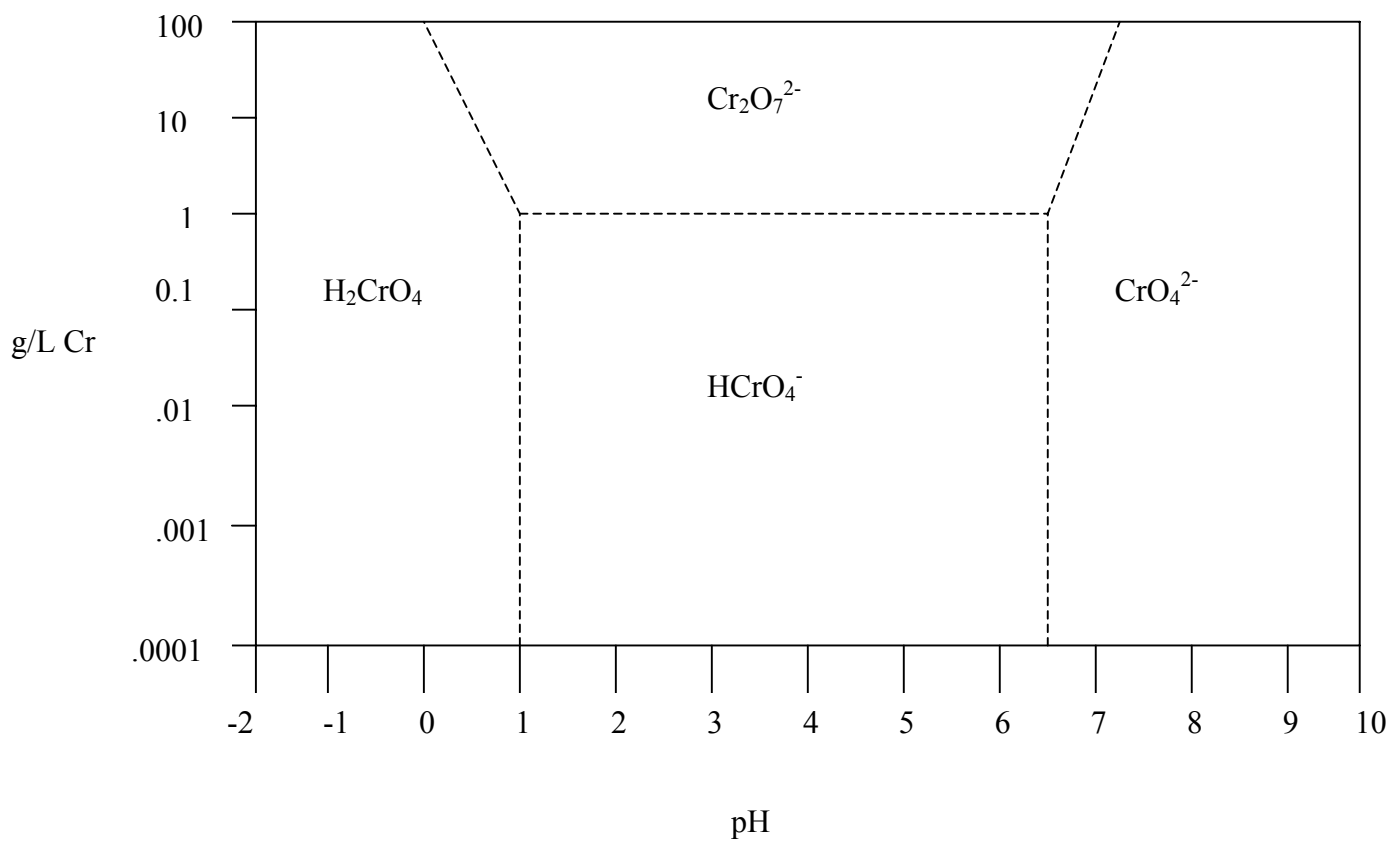
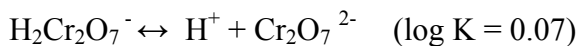
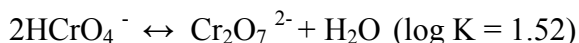
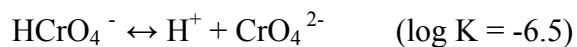
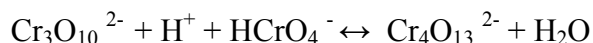
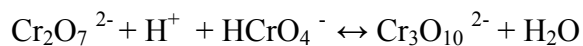


Figure 4. Relative Distribution of Cr (VI) Species in Water as a Function of pH and Cr (VI) Concentration. Reproduced from [16].



Higher forms of chromate polymers have also been reported in acidic solutions at high concentration [17].



It has been noted that higher polymers of chromate do exist at concentrations higher than 0.1M [17, 19].

Hexavalent chromium compounds are acidic [2]. The chromate ion is tetrahedral, and the structure of the dichromate ion corresponds to two tetrahedral linked through a corner oxygen. The Cr-O-Cr bond angles in the polymeric species are about 120°, and the Cr-O bond lengths of the linking Cr-O-Cr bonds are 179 pm, while the Cr-O bond lengths in the chromate and in the dichromate ions are 166 and 163 pm, respectively [2]. Figure 5 shows the structure of the chromate and dichromate anions [4]. Aqueous solutions of the hexavalent compounds absorb in the ultraviolet and violet regions of the spectrum (Figure 6). Those of the chromates are distinctly yellow, dichromates are orange, and the higher polymers are red [2]. As pH is lowered the familiar red dichromate $\text{Cr}_2\text{O}_7^{2-}$ forms, followed by formation of the tri- and tetra- anions $\text{Cr}_3\text{O}_{10}^{2-}$ and $\text{Cr}_4\text{O}_{13}^{2-}$, respectively [4]. The small size and large charge of the chromium (VI) moiety enhances its liability and engenders CrOO double bonding (infrared stretch at 730 cm^{-1}). In chromium-contaminated waters a yellow color is imparted to the water in concentrations above 1mg/L [7]. The presence of dichromates is seen as an orange color in contaminated water.

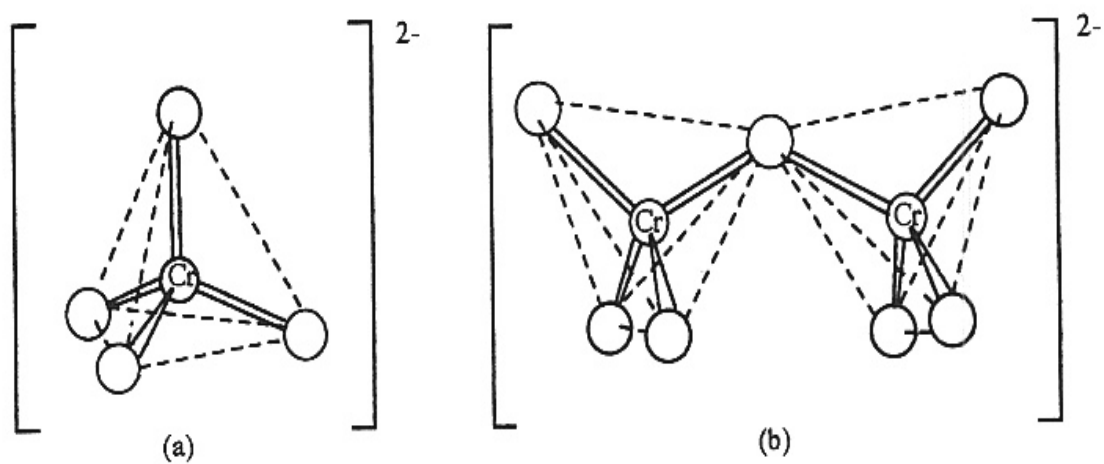


Figure 5. Structure of the Chromate and Dichromate Anions

(a) CrO_4^{2-} ion ; (b) $\text{Cr}_2\text{O}_7^{2-}$ ion. Reproduced with permission from *Environmental Health Perspectives* [4].

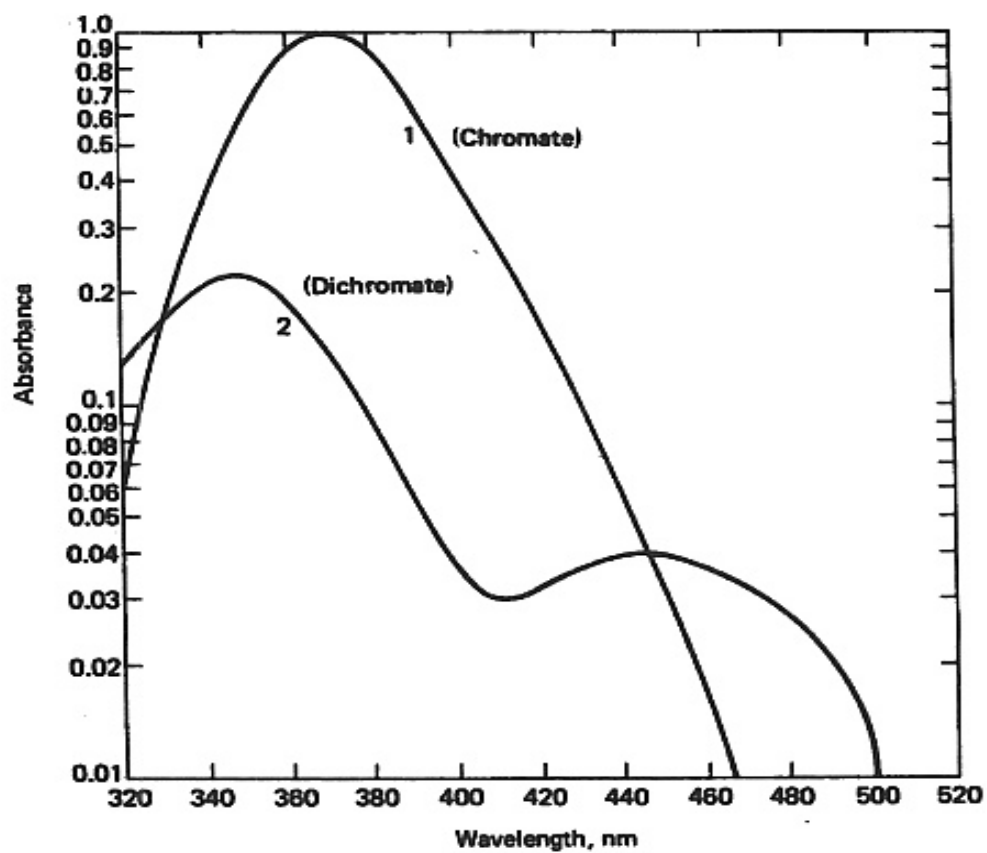


Figure 6. UV-VIS Spectra of Chromate and Dichromate.

1.6 Environmental Fate and Transport of Chromium

As chromium is weathered from minerals, most will initially be present in soil in the trivalent state, which may be adsorbed on other metal hydroxides and is not very available to plants. Weathering may accelerate the oxidation of Cr(III) to Cr(VI) through the exposure of oxidizing MnO₂ sites. [8]. Hexavalent chromium is relatively stable and mobile in soils that are sandy or contain low organic matter concentrations. The environmental transport of chromium compounds in surface waters is usually as particulates, but soluble hexavalent chromium compounds are also involved [2]. The migration of chromium compounds in soil takes place by sequential partitioning of soluble hexavalent species between groundwater and solid surfaces (Figure 7). Groundwater is the water that exists below the earth's surface in cracks and spaces in soil, sand and rocks. The area where water fills these spaces is called the saturated zone. The top of this zone is called the water table. The water table may be only a foot below the ground's surface or it may be hundreds of feet down. Groundwater is stored in, and moves slowly through, layers of soil, sand and rocks called aquifers. The speed at which groundwater flows is dependent on the size of the spaces in the soil or rock and how well the spaces are connected.

Aquifers typically consist of gravel, sand, sandstone, or fractured rock, like limestone [20]. These materials are permeable because they have large connected spaces that allow water to flow through. In areas where material above the aquifer is permeable, pollutants can sink into the groundwater. Contaminant plumes often have a vertical component of flow that carries the contaminants deeper into the aquifer while leaving the down-gradient surface soils uncontaminated (Figure 8). The release of chromium from terrestrial sediments and soils is of concern both from the fertility/phytotoxicity standpoint and from considerations of groundwater contamination/public health [2].

Gupta's triphasic soil system model, illustrated in Figure 9, provides a convenient reference frame for the terrestrial transport and fate of chromium compounds. The gas

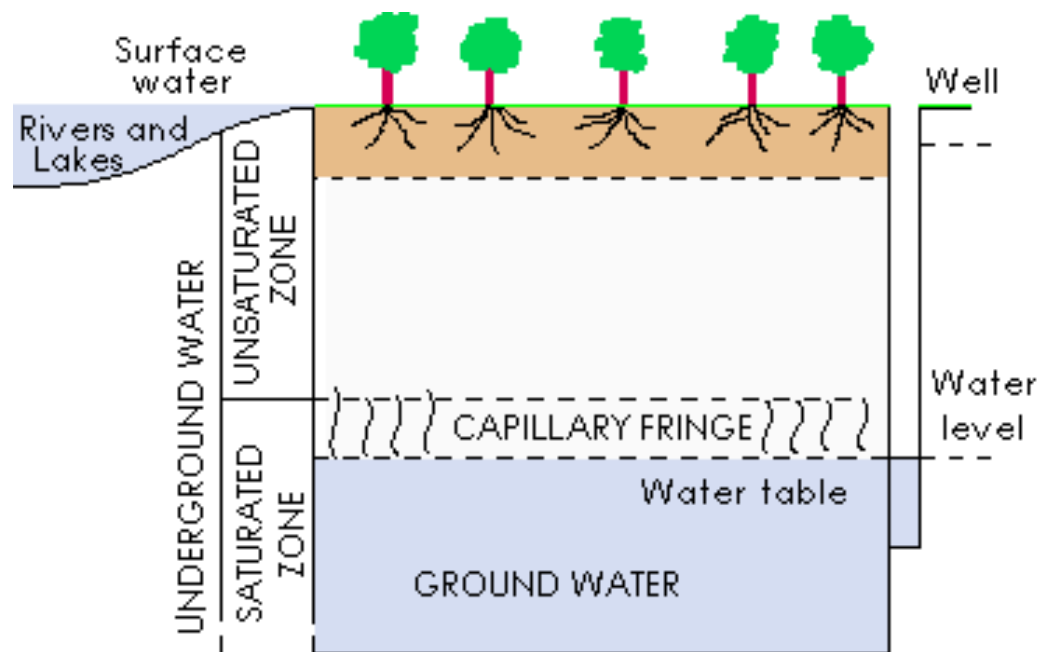


Figure 7. Schematic of Groundwater.

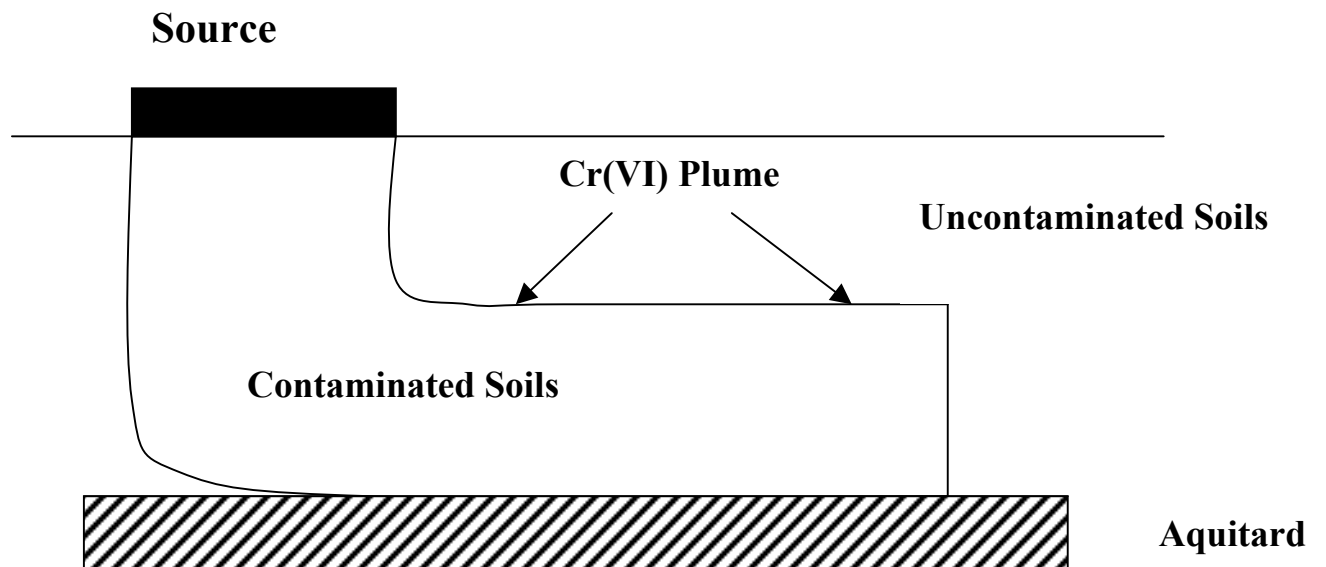


Figure 8. Chromium Plume Transported into Lower Portion of an Aquifer as a Result of Vertical Gradients (Soil above the plume is uncontaminated). Reproduced with permission from *Environmental Health Perspectives* [7].

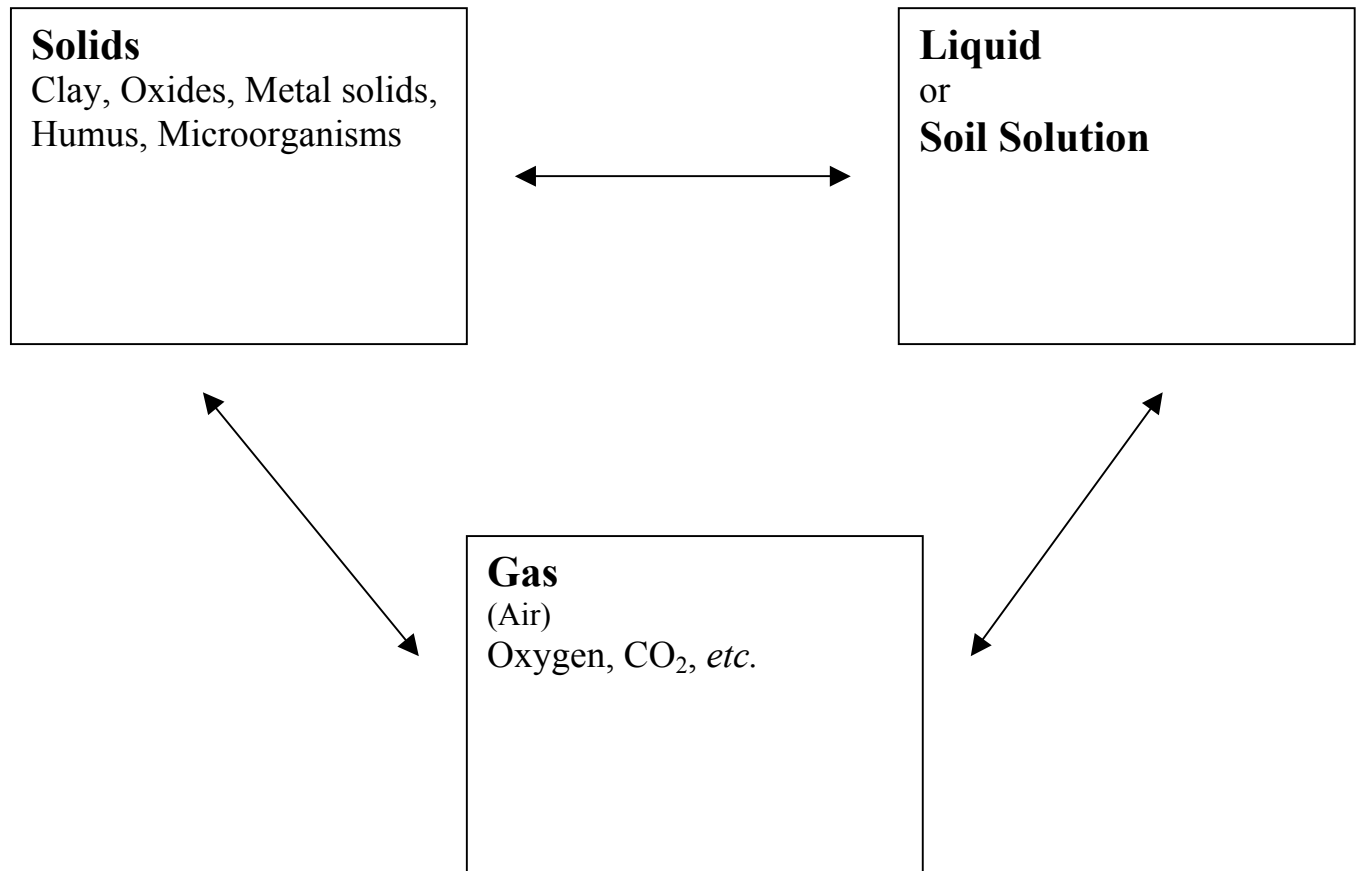


Figure 9. Triphasic Soil System

phase (soil air) is approximately 25% by volume of the soil system. The concentrations of metallic compounds are insignificant in the gas phase [2]. The solid phase includes a variety of inorganic and organic materials that constitute the skeletal framework or matrix of the soil. The liquid phase (soil solution) is approximately 25% by volume of the soil system. Clearly, transport of chromium compounds to and from the solid phase must take place via the soil solution [2]. Factors such as pH, solubility, cation and anion exchange capacity (CEC), and channel/pore size influence the transport of chromium in soil systems [2].

Complex chromium chemistry makes it difficult to predict the speciation of chromium in the environmental matrices. The environmental chemistry of chromium compounds involves oxidation-reduction transformations, precipitation-solubilization reactions, and adsorption-desorption phenomena [2]. The standard reduction potentials for the oxidation – reduction equilibria among the various valence states of chromium are summarized in Table 6 [2]. In acidic media, hexavalent chromium compounds are strong oxidizing agents; that is Cr(VI) is readily reduced to Cr(III) at low pH. At high pH, the trivalent chromium is a reducing agent and is readily oxidized to the hexavalent state [2].

Oxidation and reduction reactions can convert Cr(III) to Cr(VI) and vice versa. The coupling of oxidation and reduction reactions for chromium may be viewed as a cycle in which Cr(III) and Cr(VI) are interconverted by manganese redox cycle and oxidation of organic matter (Figure 10). Reduction reactions of Cr(VI) may occur simultaneously with oxidation of Cr(III) in heterogeneous soil materials [12]. Schroeder and Lee, in a laboratory study on the transformation of chromium in natural waters, found that Cr(III) and Cr(VI) are readily interconvertible under natural conditions [21]. Their results indicated that Cr(VI) can be reduced to Cr(III) by Fe(II), dissolved sulfides, and certain organic compounds with sulfhydryl groups, while Cr(III) can be oxidized by a large excess of MnO₂ and at a slower rate by O₂ under natural water conditions. Moreover, if aquatic conditions favor Cr(VI), then chromium will accumulate

Half-Cell Reaction	E^0 (V)	Change
$\text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{CrO}_4^{3-} + 2\text{H}^+$	0.55	VI to V
$\text{Cr}_2\text{O}_7^{2-} + 6\text{H}^+ + 4\text{e}^- \rightarrow 2\text{CrO}_2 + 3\text{H}_2\text{O}$	0.95	VI to IV
$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$	1.38	VI to III
$\text{CrO}_4^{3-} + 4\text{H}^+ + \text{e}^- \rightarrow \text{CrO}_2 + 2\text{H}_2\text{O}$	1.34	V to IV
$\text{CrO}_4^{3-} + 8\text{H}^+ + 2\text{e}^- \rightarrow \text{Cr}^{3+} + 4\text{H}_2\text{O}$	1.72	V to III
$\text{CrO}_2 + 4\text{H}^+ + \text{e}^- \rightarrow \text{Cr}^{3+} + 2\text{H}_2\text{O}$	2.10	IV to III
$\text{Cr}^{3+} + \text{e}^- \rightarrow \text{Cr}^{2+}$	-0.42	III to II
$\text{Cr}^{3+} + 3\text{e}^- \rightarrow \text{Cr}$	-0.74	III to 0
$\text{Cr}^{2+} + 2\text{e}^- \rightarrow \text{Cr}$	-0.90	II to 0
$\text{CrO}_4^{2-} + 4\text{H}_2\text{O} + 3\text{e}^- \rightarrow [\text{Cr}(\text{OH})_4]^- + 4\text{OH}^-$	-0.72	VI to III
$\text{CrO}_4^{2-} + 4\text{H}_2\text{O} + 3\text{e}^- \rightarrow \text{Cr}(\text{OH})_3 + 5\text{OH}^-$	-0.11	VI to III
$[\text{Cr}(\text{OH})_4]^- + 3\text{e}^- \rightarrow \text{Cr} + 4\text{OH}^-$	-1.33	III to 0
$\text{Cr}(\text{OH})_3 + 3\text{e}^- \rightarrow \text{Cr} + 3\text{OH}^-$	-1.33	III to 0

Table 6. Oxidation – Reduction Equilibria Among the Various Valence States of Chromium.

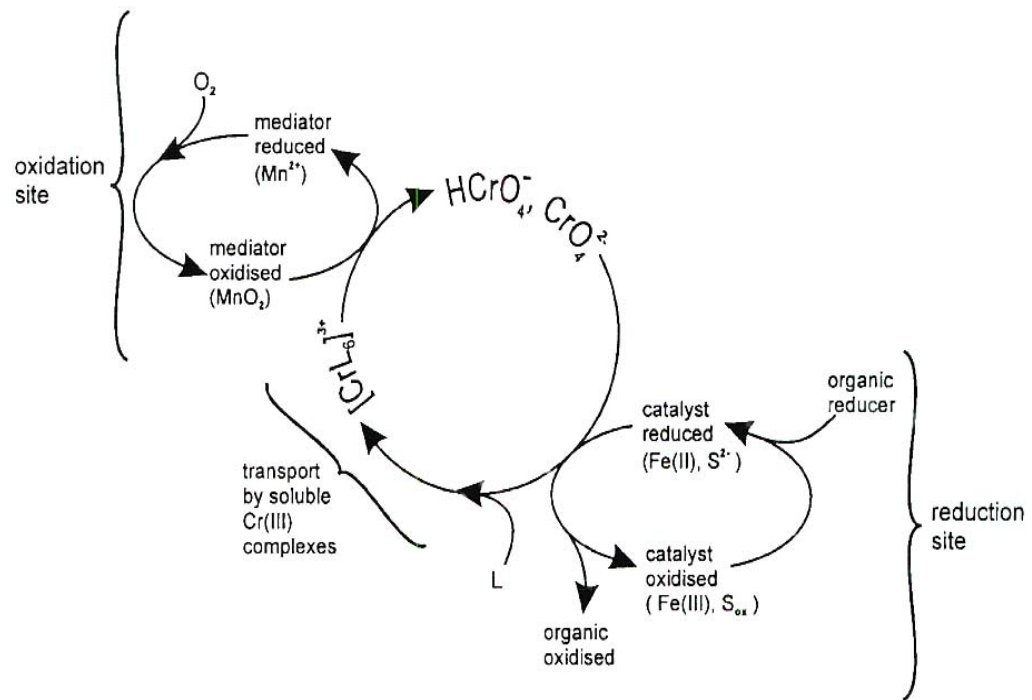


Figure 10. Interconversion Cycle of Cr(III) and Cr(VI).

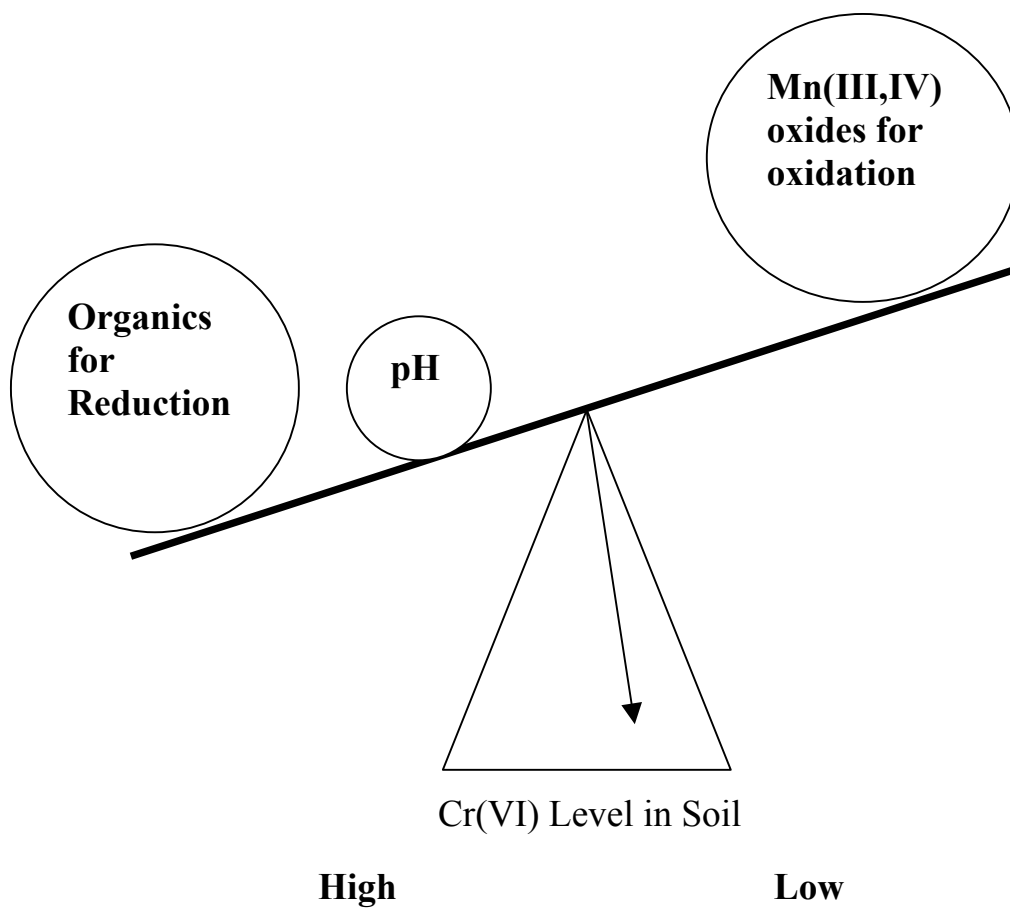


Figure 11.

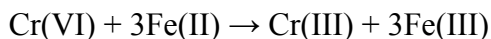
Role of pH: The balance between Cr(III) oxidation by Mn(III,IV) hydroxides and oxides and Cr(VI) reduction by organic matter in soils is affected by pH. The dynamic shifts in valence state are more significant for soluble forms of Cr(III) and Cr(VI) than for more inert and insoluble compounds [12].

as soluble forms in waters; if, however, Cr(III) is favored, then the accumulation will occur in the sediments, thus reducing its potential bioavailability [21].

The relationship between Cr(III) and Cr(VI) depends on a balance between oxidation and reduction. The soil pH is a master variable (a rolling weight on the seesaw) that controls the balance between the two opposing redox reactions (Figure 11). Reduction of Cr(VI) by organic matter and other electron donors [e.g., Fe(II) and sulfides] is favored by pH values < 6, and both oxidation and reduction may be inhibited under more alkaline conditions [12].

1.7 *Reduction of Cr(VI) to Cr(III)*

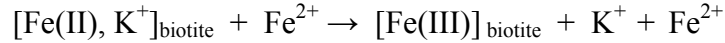
Although, Cr(VI) is not appreciably retained by the negatively charged colloids in soils, it is sorbed on many hydrous oxides. In addition to the possibility of immobilizing Cr(VI), this species can be reduced to Cr(III). This alleviates the hazard imposed by Cr(VI), but one should always consider the possibility of Cr(III) oxidation back to Cr(VI) [11]. The reduction of Cr(VI) by elemental iron can be described by the overall reaction:



This reaction is appropriate for pH less than 10 and PO_4^{2-} concentrations less than 0.1mM [7]. Above pH 10, the rate of oxidation of the ferrous iron by dissolved oxygen is greater than rate of oxidation by ferrous iron by CrO_4^{2-} [7]. PO_4^{2-} is known to increase the rate of oxidation of Fe(II) by dissolved oxygen. The Cr(III) and Fe(III) can hydrolyze, combine, and precipitate in solid solution series. This reaction has been found to be very rapid with equilibrium being established in less than 5 min even in the presence of dissolved oxygen [7].

Fe(II) is not always present in significant concentrations in subsurface waters, however, a major source of Fe(II) may be found in mineral phases that are present in geologic units. For example, the minerals hematite and biotite (which contains some FeO) are capable of reducing Cr(VI) [7]. On both mineral phases, the reduction of Cr(VI) appears to be occurring in the solution and not at the mineral surface itself. Therefore, the rate of reduction of Cr(VI) depends on the rate of dissolution of the FeO component in

the mineral phases. For biotite, it is suggested that once the Fe(II) has been oxidized, the resulting Fe(III) reacts with the Fe(II) in the mineral according to:



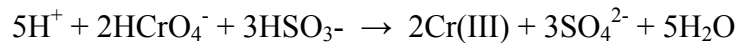
This reaction can be driven by the continual oxidation of the Fe(II) by Cr(VI) [7]. This Fe(II)_{aq} ion is then available for the further reduction of Cr(VI). The resulting Fe(III) is reduced at the surface of the biotite, continuing the cycle. The rate of reduction of Cr(VI) by hematite and biotite increases with increasing ratio of surface area to solution volume and is greater under acid conditions than under neutral or alkaline conditions[7].

Other common mineral phases may be effective in reducing Cr(VI) to Cr(III) in the subsurface. For example, iron sulfides can be excellent sources of ferrous iron. The observation that iron in the octahedral sites of iron-rich smectite can be readily oxidized by O₂ and reduced by sodium dithionite (Na₂S₂O₄) suggests that the octahedral iron may also reduce Cr(VI) [7]. Other phyllosilicates such as chlorite contain significant amounts of ferrous iron that may reduce Cr(VI) in a manner similar to biotite [7].

Cr(VI) can be reduced by sulfur compounds such as sulfide and sulfite. Although sulfide can reduce Cr(VI), studies indicate that ferrous iron must be present to act as catalyst. This suggests that iron sulfide minerals in some aquifer materials may effectively reduce Cr(VI). In the presence of excess sulfite, the reduction of Cr(VI) follows the reaction [7]:



The S₂O₆²⁻ can then reduce ferric iron if it is present. The reduction in the presence of excess Cr(VI) follows:



These reactions are believed to occur in one-step, three-equivalent reductions [7].

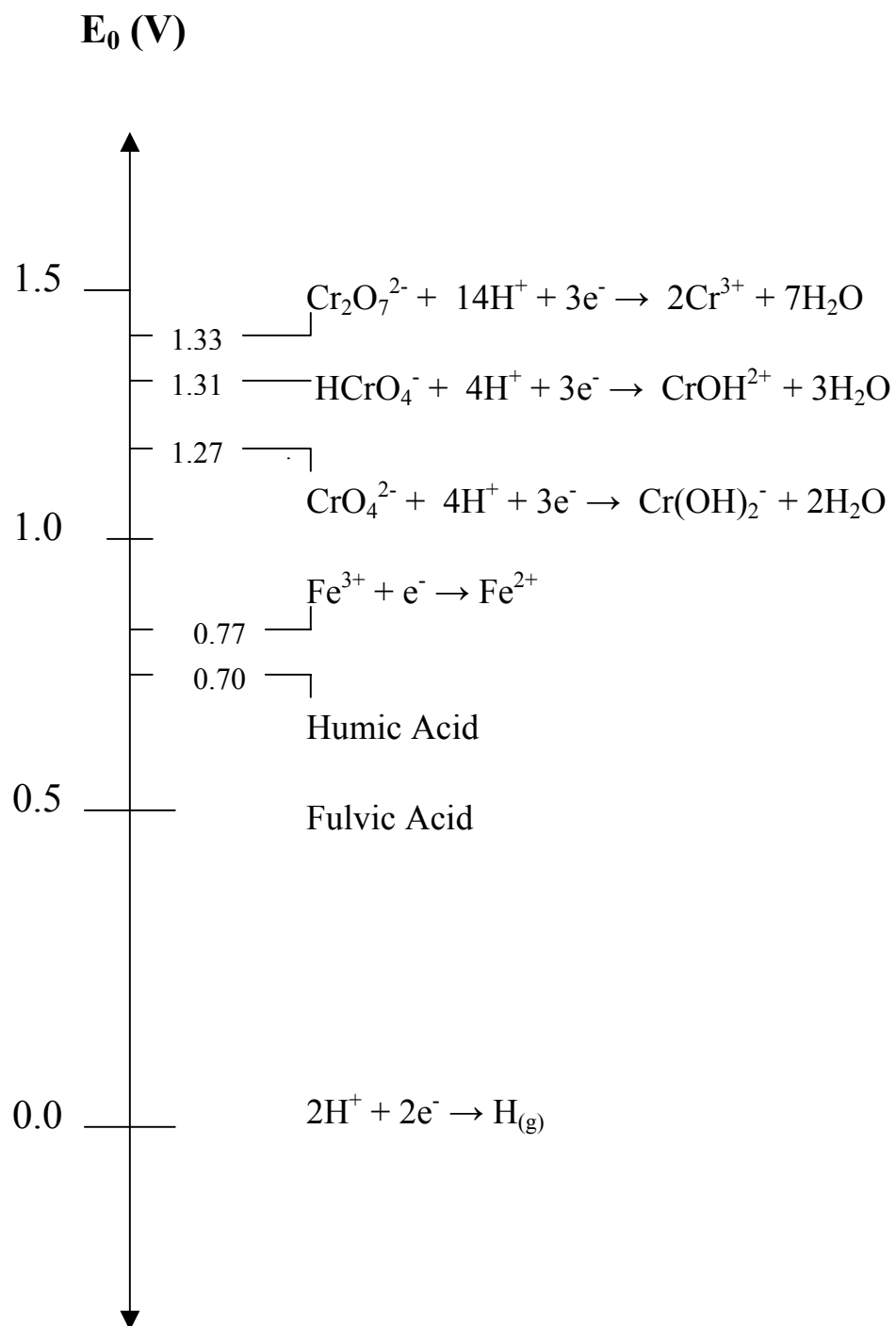
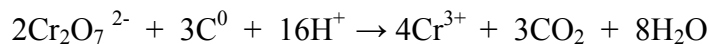


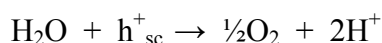
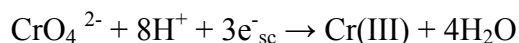
Figure 12. Standard electrode potentials for key reactions involving the reduction of chromium. Reproduced with permission from *Environmental Health Perspectives* [7].

Another important soil constituent that contributes to the reduction of Cr(VI) in the subsurface is soil organic carbon (SOC). The amount of reduction of dichromate by soil is often used as a measure of SOC. The overall reaction can be idealized as [7]:



The reaction consumes hydrogen ions and therefore is likely to be more rapid in acidic environments than in neutral or alkaline environments [7]. Cr(VI) is reduced by functional groups such as carboxylic acids, alcohols, and phenols commonly found in humic substances or as contaminants in association with chromium. In many soils, a substantial fraction of SOC is in the form of humic substances: humic acid (HA), humin, and fulvic acid (FA) [7]. Investigations reveal that FA and HA reduce a variety of metal ions. Redox reactions involving HA and FA have been studied for a number of redox couples Hg(II)/Hg(0) and Mo(VI)/Mo(IV). Reports of the standard reduction potential, E_0 , for FA and HA indicate that FA is a better reducing agent than HA and that both have the potential for reducing Cr(VI) (Figure 12) [7].

The presence of SOC reduces Cr(VI) above pH 7.0. Bartlett and Kimble found that reduction did not occur in an essentially organic free soil unless an external source of organic matter was added *i.e.* cow manure [7]. Even then reduction did not occur until pH was lowered. They state that soil organic matter is more effective than cow manure at reducing Cr(VI). This observation may indicate that as organic matter becomes more “humified” it develops more reactive reducing sites. Bloomfield and Pruden found that water soluble soil organic matter was effective in reducing hexavalent chromium at pH less than 4 but not effective at pH greater than 5 [7]. Adsorbed forms of Cr(VI) are, in some cases, more easily reduced than soluble forms in limed soils. The addition of fulvic acid to groundwater samples spiked with Cr(VI) showed significant reduction, particularly in acidified samples. The rate of reduction was much less at 4°C than at 25°C [7]. The reduction of Cr(VI) can also occur as a result of photoreduction reactions. Studies of photoreduction of Cr(VI) on ZnO in neutral to alkaline solutions have shown that large percentages of Cr(VI) can be reduced (30-70%) [7]. The reaction likely occurs as the two half-cell reactions:



Where sc denotes semiconductor and h^+_{sc} denotes a “hole” in the semiconductor where electrons have been displaced. The percentage of Cr(VI) that is photoreduced is not greatly influenced by SO_4^{2-} , NO_3^- , or Cl^- , and other anions but is influenced by the cations in solution [7].

ZnO is not commonly found in streams and other surface waters, but these results indicate that photoreduction of other semiconductors such as iron oxides is possible. Amorphous ferric hydroxides and aqueous ferric iron present in streams may be photoreduced to ferrous irons [7]. The ferrous iron would then be available for oxidation by either dissolved oxygen or Cr(VI). For pH less than 10, the rate of oxidation by Cr(VI) is greater than the rate of oxidation by dissolved oxygen, therefore most of the ferrous iron could be used for the reduction of Cr(VI) [7].

Aside from reduction mechanisms of Cr(VI), reactions exist that immobilize Cr(VI) which do not alter its toxicity but they decrease the risk imposed by this ion. The environmental risk of sorbed Cr(VI) is then dependent on the sorbates stability [11]. Hydrous oxides of Al and Fe are often present at significant levels in surface environments; they commonly have a net positive charge and a chemical affinity for Cr(VI). Modeling efforts of Cr(VI) sorption on hydrous oxides of Fe and Al, as well as in soils, suggest that Cr(VI) forms an outer-sphere complex on these surfaces (Figure 13) [11]. Competitive ion displacement studies have shown that Cr(VI) is retained much more strongly than Cl^- and SO_4^{2-} and that its retention strength approaches that of phosphate. Accordingly, the risk invoked by this ion can be significantly attenuated by its retention on such materials. In soils with low levels of Al and Fe hydrous oxides on should be aware that there may be a very low capacity for Cr(VI) sorption [11].

1.8 Oxidation of Cr(III) to Cr(VI)

Oxidation of Cr(III) to Cr(VI) represents a significant environmental hazard since a rather innocuous species is transformed into a toxic one. While there are many potential

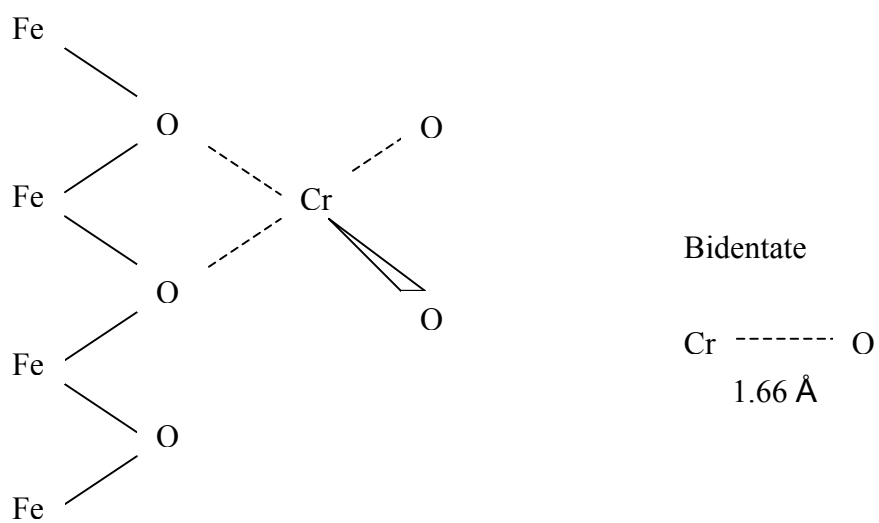
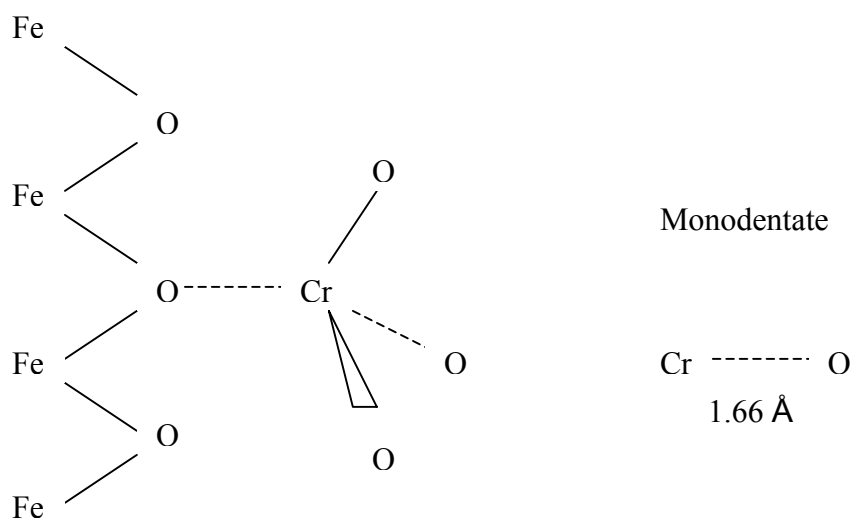
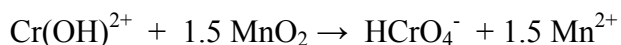


Figure 13. Surface Complexation Structure of Cr(VI) on Iron Hydroxide. Reproduced from [11].

mechanisms for the reduction of Cr(VI) to Cr(III), the potential mechanisms for the oxidation of Cr(III) to Cr(VI) appear to be limited to oxidation by oxygen or by manganese oxides. However, recent studies have found that oxygen does not react appreciably with Cr(III) [7]. Bartlett and James observed the correlation between the amount of Cr(III) oxidized by soils and the amount of hydroquinone-reduced manganese in the soils. They found that Cr(III) was not oxidized in dry soils but it is oxidized in soils that are maintained in moist conditions. The drying of soils alters the surface of the manganese oxides by reducing the manganese and decreasing its ability to oxidize Cr(III) [7]. The rate and amount of Cr(III) oxidation by β -MnO₂ (pyrolusite) increases with increasing ratio of surface area to solution volume and with decreasing pH. In these same tests, it was observed that oxygen does not catalyze the reaction between β -MnO₂ and Cr(III) [7]. The stoichiometry of the oxidation of Cr(III) by β -MnO₂ is complex, and the exact reaction mechanism is not known but believed to follow the general reaction:



It is suggested, however, that the desorption of HCrO_4^- and the formation of a secondary manganese phase (MnOOH) may play important roles in the oxidation of Cr(III) [7].

To show the conditions of pH and potential under which each species is thermodynamically stable, a Pourbaix diagram is useful. The Eh-pH diagram presented in Figure 14 shows the chromium species dominant under equilibrium conditions and their potentials for oxidation-reduction [2]. The boundaries in the figure shift with ionic strength and temperature but it is a reasonable demarcation between the dominant aqueous forms [7]. From thermodynamic considerations it is obvious that Cr(VI) may exist naturally in soils [8]. The solubility of trivalent chromium is very low at the pH values typical for most soils. The influence of pH on the solubility of trivalent chromium is shown in Figure 15. At a pH of 4, trivalent chromium is almost equally distributed between the two cationic species $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ and $[\text{Cr}(\text{H}_2\text{O})_5\text{OH}]^{2+}$. From pH of 6.3 to

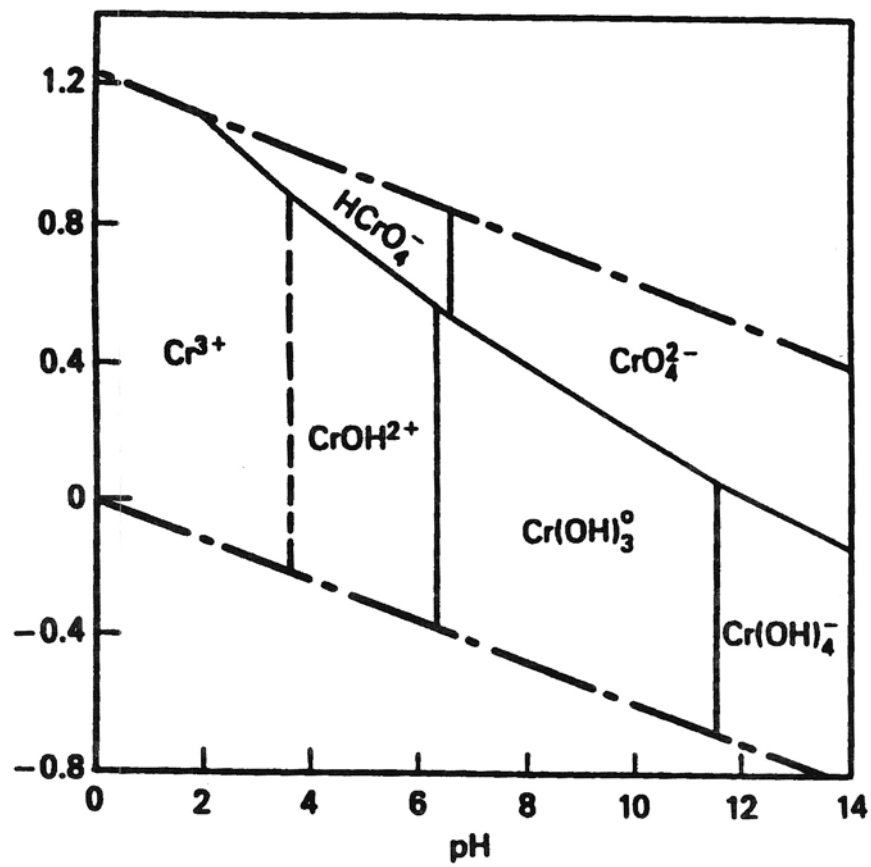


Figure 14. Eh-pH Diagram for Various Chromium Species. Eh is the Oxidation-Reduction Potential.

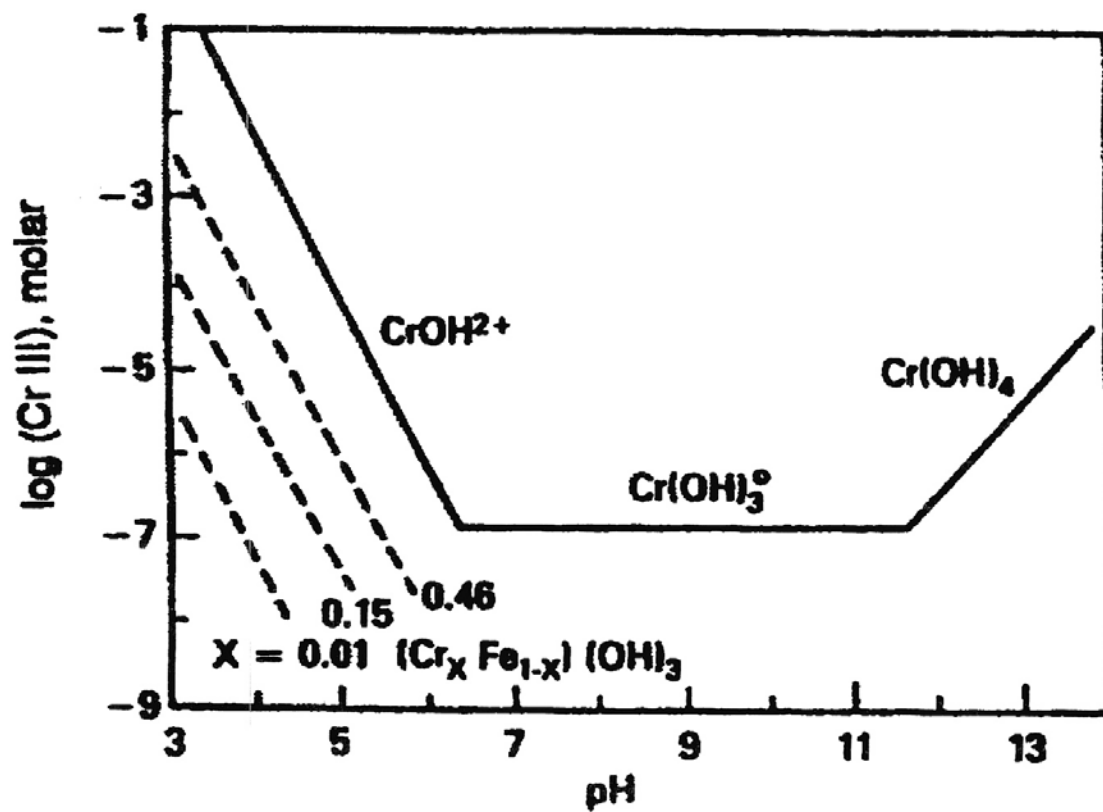
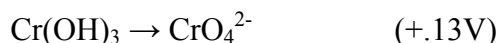


Figure 15. pH-Solubility for Various Chromium Species.

Couple	Equation	E° Volts
Cr(0)-Cr(II)	$\text{Cr} \rightleftharpoons \text{Cr}^{+2} + 2\text{e}^{-}$	0.86
Cr(0)-Cr(III)	$\text{Cr} \rightleftharpoons \text{Cr}^{+3} + 3\text{e}^{-}$	0.71
	$\text{Cr} + 3\text{OH}^{-} \rightleftharpoons \text{Cr}(\text{OH})_3 + 3\text{e}^{-}$	1.3
Cr(II)-Cr(III)	$\text{Cr}^{+2} \rightleftharpoons \text{Cr}^{+3} + \text{e}^{-}$	0.41
Cr(III)-Cr(VI)	$2\text{Cr}^{+3} + 7\text{H}_2\text{O} \rightleftharpoons \text{Cr}_2\text{O}_7^{-2} + 14\text{H}^{+} + 6\text{e}^{-}$	-1.36
	$\text{Cr}(\text{OH})_3 + 5\text{OH}^{-} \rightleftharpoons \text{CrO}_4^{-2} + 4\text{H}_2\text{O} + 3\text{e}^{-}$	0.12

Table 7. Chromium Oxidation Potentials.

11.5, the insoluble $\text{Cr}(\text{OH})_3$ is the dominant form of trivalent chromium. Above pH 12, the anionic form $[\text{Cr}(\text{OH})_4]^-$ is formed. The adsorption-desorption exchanges of soluble chromium compounds are also pH dependent [2]. In its highest oxidation state chromium(VI) forms exclusively oxy compounds and all are potent oxidizing agents. In basic solution the chromate ion is less oxidizing:



than the dichromate ion in acidic solution



In aquatic environments, the primary types of reactions into which chromium enters the system are oxidation-reduction reactions. Table 6 presents the oxidation potentials for chromium [5]. Based on the above information it is apparent that chromium in an aquatic environment may be present in either dissolved or particulate state [5]. Most dissolved chromium is Cr(VI) and is most often found when pH is neutral or acidic. Cr(VI), which is a strong oxidizing agent when present in an anionic complex, readily oxidizes organic material. The result of this oxidation is reduced chromium (Cr^{3+}), which is readily hydrolysable. Hydrolysis produces insoluble chromium hydroxides that readily precipitate [5].

1.9 Analytical Determination of Chromium

Various industries assert that environmental regulation efforts should be focused on Cr (VI) instead of Cr (III). However, whether one wants to determine one or both species in a sample, the analytical method must be capable of differentiating between the two [6]. For chromium in natural waters, most speciation studies deal with the determination of the total amount of dissolved Cr(III) and Cr(VI), owing to the different interactions of these two forms with living organisms [23]. Speciation of various oxidation states of a metal in a sample is a difficult process. Even after an analytical method has been developed, the question of whether or not the sample preparation procedure altered the natural state of the species still remains. These problems combine to make an even more difficult situation. To date, the study of sampling for the speciation of chromium is an area of considerable activity [6]. Advances in understanding the fate of

chromium in the environment depend on the accurate determination of chromium species in aquatic systems.

A detailed knowledge of each species rather than the total Cr level is required to properly evaluate physiological and toxicological effects of Cr, its chemical transformations in water, soil and atmosphere as well as its distribution and transport in the environment [9]. A major obstacle in the determination of chromium in natural waters is the preservation and stabilization of the natural speciation state of the sample. The stability of chemical species in environmental samples is a critical factor during storage, owing to the interconversion and degradation processes which can occur in species characterization [24]. Another problem that arises in the determination of chromium in waters is due to its low concentration. In addition to the need of a very sensitive method, contamination, sorption, and species alteration can cause extremely large analytical errors [8].

Analysis of environmental matrices for chromium speciation should be performed as soon as possible after sampling to avoid degradation, sorption, complexation and interconversion. The preservation and stabilization (maintaining oxidation state) of these chemical species in the time interval between sampling and analysis is difficult and several studies have been developed to improve the quality of speciation analysis [24]. The concentration range in which Cr can be either essential or toxic is very narrow, hence the need for accurate analytical methods. There are a number of sampling issues associated with metal species such as stabilization, absorption, complexation, and filtration that need to be addressed in order to maintain a representative sample [2]. Few studies demonstrate the ability to stabilize and preserve individual fractions, thus laboratory measurements may not reflect the actual concentrations of species at the time of sampling [3].

Speciation analysis is particularly demanding when applied to trace elements. Here, the analytical difficulties are not only related to the choice of relevant analytical techniques for measuring the individual species, but also to the fact that even the total

concentration is extremely difficult to determine. A further fractionation is rarely possible, unless preconcentration techniques, which will not disturb the distribution of the species, are used [14]. Elements in trace amounts, which require separation, are often found in matrices of other species, which complicate their separation [4].

Speciation analysis of trace heavy metals in environmental samples concerns their presence in various oxidation states, in different protonated and polymerized forms, in complexes with various ligands and various degrees of homogenous association with constituents of natural samples [23]. An effective separation of trace heavy metals requires that there be sufficient specificity by the system used (containing the extractant and metal ion) for that element over other closely related elements even if these elements are present in high concentration. Secondly, the affinity of the extractant for the ion of interest must be sufficiently high so that low levels of the ion can be efficiently removed from the solution. Thirdly, the separations system is often required to remove trace amounts of ions from large volumes of solution, which is difficult using conventional procedures. This difficulty arises from the need to obtain rapid separation kinetics. Slow kinetics arise from slow diffusion rates and slow association-dissociation rates between the extractant and metal ion [4].

A search of literature shows that many methods are available for the determination of total chromium, and some can also evaluate oxidation state and species [4]. In the last decade, various analytical methods have been developed in order to separate and determine Cr(III) and Cr(VI) species in different biological as well as environmental samples. These include ion-exchange methods, spectrophotometric methods, and capillary electrophoresis [14] as shown in Table 7. Direct flow injection systems combined with atomic absorption spectrometry (AAS) or inductively coupled plasma mass spectrometry (ICP-MS) have also been utilized [14]. Supported liquid membranes (SLMs) have been used for the removal of Cr(VI) from groundwater and tannery effluent. However, the use of SLM technology for analytical trace metal analysis has been limited.

There are two main groups of Cr speciation methods: off and on-line [3]. Off-line methods involve separation and pre-concentration of a particular Cr species before sample insertion into the detection instrument. The sample pre-treatment techniques include: (1) colored complex formation methods, (2) chromatographic methods, (4) electrochemical methods, (5) co-precipitation techniques, (6) ion-exchange techniques, (8) separation using chelating resins, (9) and solvent extraction [3]. For detection, the spectroscopic methods are generally used, including mainly UV-VIS spectrometry, atomic absorption spectrometry (AAS)/electrothermal atomic absorption (ETAAS) and inductively coupled plasma atomic emission spectrometry (ICP-AES) [3]. These methods have, however many disadvantages: they are complicated, time consuming, affecting mostly Cr speciation, resulting often in losses of the analyte and/or contamination problems. Additionally, problems inherent to manual sample manipulation result in off-line methods not being really quantitative and their efficiencies are often low [13].

On-line techniques are preferable because they are relatively fast and require minimal sample pre-treatment. The high costs of the instruments however limit their wide application to environmental analyses [13]. On-line methods couple the separation system with the detection system; in consequence separation, identification and quantification of Cr are carried out in a one-step analytical process. Among the main separation-speciation techniques are: flow injection analysis (FIA) and high performance liquid chromatography (HPLC), which includes ion chromatography (IC), and ion-pair chromatography (IPC) and reversed phase chromatography (RP) [13]. The FIA separation process is similar to batch filtration or solvent extraction procedures where separation columns are filled with: (1) cellulose sorbents; (2) chelation ion exchanger; (3)

Table 8. Spectroscopic Analytical Methods in the Determination of Cr(III) & Cr(VI).

Determined species	Detection technique	Separation method	Application
Cr(III)	FAAS	Graphite tube electrodeposition	Seawater
Cr(VI)	ETAAS	Anion exchange	Welding fumes
Cr(III)	UV-Vis	Cation exchange	Natural waters
Cr(VI)	UV-Vis	Solvent extraction	Steel sample
Cr(VI)	FAAS	Solvent extraction	Seawater

FAAS, flame atomic absorption spectrometry; ETAAS, electrothermal atomic absorption spectrometry; UV-Vis, ultra violet-visible photometry

Table 8 (cont'd). Off-line Analytical Methods in the Determination of Cr(III) & Cr(VI).

Determined species	Detection technique	Separation method	Application
Cr(VI)	FIA-UV	Alumina (acidic form) DPC	Mineral water
Cr(T)	FIA-ETAAS	DDTC/C ₁₈	Drinking water
Cr(III)	FIA-FAAS	Chelating resin (PHXA)	Seawater
Cr(VI)	FIA-ICP-AES	Alumina (acidic form)	Synthetic water
Cr(III)	FIA-ETAAS	Alumina (SDS-coated)	Lake water

FIA, flow injection analysis; FAAS, flame atomic absorption spectrometry; ETAAS, electrothermal atomic absorption spectrometry; UV-Vis, ultra violet-visible photometry; DPC, 1,5-diphenylcarbohydrazide; DDTC, diethyldithiocarboonate; APDC, ammonium pyrrolidithiocarbonate; PHXA, polyhydroxa-amic acid; SDS, sodium dodecyl sulphate

Table 8 (cont'd). Analytical Methods in the Determination of Cr(III) & Cr(VI).

Determined species	Detection technique	Separation method	Application
Cr(III)	IC-UV	Anion exchange/DPC	River water
Cr(VI)	IC-FD	Anion/cation exchange/luminol	Synthetic mixture
Cr(III)	IPC-UV	PAR/TBAI	Synthetic mixture
Cr(VI)	RP-HPLC-UV	C ₁₈ /DPC	Drinking water
Cr(III)	RP-SPE-HPLC-UV	C ₈ /APDC	Standard reference

IC, ion chromatography; UV-Vis, ultra violet-visible photometry; FD, fluorescence detector; IPC, ion pair chromatography; RP, reversed phase; HPLC, high performance liquid chromatography; DPC, 1,5-diphenylcarbohydrazide; APDC, ammonium pyrrolidithiocarbonate; PAR, 4-(2-pyridylazo)resorcinol; TBAI, tetrabutylammoniumiodide

complex-forming resin; (4) C-18 bonded silica; (5) polyether ether ketone; and (6) activated or modified alumina [13]. Uncompleted recovery of a given species from solid sorbents, competition with other ions on the columns, spectral interferences from co-eluted ions originating from sample and/or column packing are the main problems inherent in FIA.

HPLC is a convenient technique for the simultaneous determination of both Cr(III) and Cr(VI) species where anion exchange columns are used on which Cr(VI) species are retained directly and Cr(III) either passes without any retention or is retained after its conversion into a negatively charged complex [13]. Retention of the two oxidation states of chromium can also be achieved in the system with both cation and anion exchange columns in parallel. These systems are, however, not widely applied for routine analysis due to high instrument costs [13]. Another major problem is the detection, which is often not sensitive enough to match the analyte level in a real sample.

Capillary electrophoresis offers better separation efficiency than chromatographic techniques. The major problem in its application is the small sample volume (several nanoliters) that requires a very sensitive detector to match naturally occurring analyte levels [13]. Electrochemical techniques, which enable simultaneous separation and determination of a given Cr form, suffer from low sensitivity.

Despite the significant advances that have been made in metal speciation analysis techniques over the past 25 years, much remains to be done. Published papers on Cr speciation generally demonstrate high sensitivity and selectivity but there is an urgent need for reproducible sampling and sample preparation, good separation, and metal species preservation [13]. The lack of analytical procedures for sample storage and individual species preservation precludes the development of routinely acceptable speciation methods. To minimize perturbation of the systems like anoxic waters, the sediment-water interface and colloidal materials, some new analytical methods for Cr species determination *in-situ* must be developed [13]. A method leading to reliable Cr

speciation involving field sampling combined with immediate Cr(III) and Cr(VI) separation is needed. This work introduces such a technique.

The present study avoids problems associated with stabilization and preservation of individual fractions of chemical species in solution. In contrast to existing methods that have severe stability, economic, and technical problems we are demonstrating a novel technique for the *in-situ* sampling, selective extraction of Cr(VI) and Cr (III) species, preservation and subsequent analysis of these fractions. This work presents an innovative method of selective ion sampling employing the use of extractant impregnated membranes. The extractants tricaprylmethylammonium chloride (Aliquat-336) and di-(2-ethylhexyl) phosphoric acid (DEHPA) were used for the selective removal and enrichment of the anionic Cr(VI) and cationic Cr (III) species, respectively. Separation of Cr(VI)/Cr(III) species by the extractant impregnated membranes was followed by standard metals analysis utilizing Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) and ultraviolet visible spectroscopy for the determination of Cr(III) and Cr(VI) species, respectively.

1.10 Summary

Cr is naturally found in rocks, soils, plants, animals, and in volcanic dust and gases. Natural contributions to the total concentrations of chromium in the environment are complemented by somewhat (~50%) larger quantities of chromium released by human activities. Anthropogenic sources originate from metallurgy, chemical, coal, and refractory industries. The inorganic chemistry of chromium is rich in its variety of oxidation states. Chromium is a metal ion that persists in the environment as either Cr(III) or Cr(VI) and depending upon its oxidation state; may be considered toxic or essential to living organisms. Chromium (III) is an essential nutrient in our diet and considered to be a trace element required for the proper functioning of living organisms through its control of glucose and lipid metabolism in mammals. In contrast, chromium (VI) is considered to pose the greatest human health risk because it is more toxic, more mobile, and more soluble than Cr(III). It serves no useful biological purpose to living things and has been found to be acutely toxic, carcinogenic, and teratogenic. The contrast in

behavior between Cr(III) and Cr(VI) has become the reason it is critical to differentiate between both oxidation states when analyzing environmental samples.

Complex chromium chemistry makes it difficult to predict the speciation of chromium in the environmental matrices. The environmental chemistry of chromium compounds involves oxidation-reduction transformations, precipitation-solubilization reactions, and adsorption-desorption phenomena. Speciation of various oxidation states of a metal in a sample is a difficult process. A major obstacle in the determination of chromium in natural waters is the preservation and stabilization of the natural speciation state of the sample. The stability of chemical species in environmental samples is a critical factor during sampling, storage, and pretreatment owing to the interconversion and degradation processes which can occur in species characterization.

The review of literature presented in this Chapter has introduced the complexity of chromium chemistry, its source, fate and transport in the environment. Elements such as chromium dominate speciation studies in the search for sampling methods, which can preserve and stabilize individual fractions upon sample collection. In the last decade, various analytical methods have been developed in order to separate and determine Cr(III) and Cr(VI) species in different environmental samples. These include ion-exchange methods, spectrophotometric methods, and capillary electrophoresis. Many methods lack the capabilities of *in-situ* sampling, separation, stabilization and preservation of individual fractions. The scarcity of literature concerning the sampling, transport, and stabilization/preservation of chromium species has led to the search for new technologies capable of the proper handling of chromium samples and isolating individual fractions. Selective ion sampling employing the use of extractant impregnated membranes offers such a technique and is discussed in further detail in Chapter 2 of this work.

Chapter 2

2. Extractant Impregnated Membranes

2.1 *Introduction*

This chapter will give a brief overview of the historical emergence of extractant impregnated membranes, the preparation methods used in creating extractant impregnated membranes, the extraction processes occurring with the extractants Aliquat-336 and DEHPA, and the theory behind these extraction processes. The need for more specific systems for metal recovery, from both ecological and economic aspects, has led to the development of new chemical techniques. Conventional analytical methods capable of sample collection, separation, and determination often do not preserve and stabilize each fraction. Sampling, storage and pretreatment may alter the natural speciation state of the sample due to interconversion and degradation processes occurring. Therefore, laboratory measurements may not reflect the actual concentrations of species at the time of sampling.

Developing analytical strategies for chromium sampling, separation and subsequent determination is a complex and controversial task and is an area requiring more study. Extensive literature research indicates that there are many techniques that focus on the tasks of separation and determination of chromium but none exhibit the capabilities of *in-situ* sampling, separation, stabilization and preservation of individual fractions. The introduction of extractant impregnated membranes in the area of speciation analysis is innovative. The principles upon which are based on conventional extraction techniques widely recognized by the analytical chemistry community.

2.2 *Historical*

2.2.1 *Solvent extraction*

During recent years, the application of different solvent extraction methods for chromium removal and concentration has been widely studied; conventional liquid-liquid extraction [25], emulsion liquid membranes [26, 27], and supported liquid membranes [28, 29] are some of the new alternatives reported in literature [30]. Solvent extraction has received a great deal of attention, especially for the treatment of solutions with high relative metal concentrations. An aqueous solution containing the analyte(s) of interest is mixed with an organic phase containing a liquid ion exchanger. After the transfer from the aqueous phase to the organic phase, both phases are separated. In the following re-extraction the loaded phase is regenerated with an aqueous phase. The method is particularly useful in the areas of preconcentration and the removal of interferences. The advantage here is the great variety of liquid ion exchangers (which can be combined) leading to a great range of possible applications [31]. The major drawback of these processes is the dispersion of the solvent: this loss has environmental and economic implications [32]. Other disadvantages are that many theoretical stages are needed for extraction from dilute effluents. This re-extraction leads also to solutions of low heavy metal concentration so the metal content has to be enriched [31].

Solvent extraction is often used in the remediation of contaminated sites through the use of organic solvents, which remove toxic metals and mixtures of metal and organic compounds. It is commonly used in combination with other technologies, such as solidification/stabilization, incineration, or soil washing. Solidification/stabilization techniques, involve locking the contaminant in the soil. This process does not chemically change the contaminant, but rather it encapsulates it [33]. Solidification/stabilization techniques reduce the mobility of hazardous substances and contaminants in the environment by physical means. These techniques can be used alone or combined with other treatment and disposal methods, such as solvent extraction. Incineration involves the use of high temperatures, 870 to 1,200 °C (1,400 to 2,200 °F), which is used to volatilize and combust halogenated and other organics in hazardous wastes [33]. Auxiliary fuels are used to initiate and sustain combustion. This technique is often used

alone or combined with other treatment and disposal methods, such as solvent extraction. Soil washing uses water to remove contaminants from soils. The process works by either dissolving or suspending contaminants in the wash solution [33]. Soil washing separates soil by particle size. Most organic and inorganic contaminants tend to bind and sorb to clay, silt, and organic soil particles. Most silt and clay are stuck to larger particles (*i.e.* sand and gravel). Washing separates the small particles from the large particles by breaking adhesive bonds. The separated material is smaller in volume and is more easily disposed of [33].

Solvent extraction gives a number of environmental benefits. It offers a route to pure metal, which avoids pollution characteristic of metallurgic processing. It also offers the opportunity to remove metals for reprocessing and redistribution [34]. On the other hand, solvent extraction may discharge effluents, which contain both organic and inorganic compounds that may be environmentally undesirable.

2.2.2 *Ion exchange*

The liquid-liquid extraction (solvent extraction) and liquid-solid extraction (resin ion exchange) methods involve similar chemical principles, but differ in technological principles. Ion exchange involves functional groups of organic polymers, which bind cations and anions [31]. These ion exchange resins are loaded semi-continuously in fixed beds. Afterwards they are regenerated with an acid or base and rinsed with water till neutral [31]. The solid ion exchange method offers greater simplicity in equipment and operation, particularly since the introduction of the continuous ion exchange concept and processes [34]. The advances in the ion exchange technology mentioned above enable the treatment of composite solutions and complicated problems. Ion exchange enables effluents from a wide variety of plants to be freed from metallic and other contaminants at reasonable cost. Unfortunately, the advances in ion-specific resins have not paralleled technological pace of development [34]. Disadvantages include the small range of possible applications, compared with reactive extraction. The choice of a suitable ion exchange resin is also often difficult, since the resins can be either high loaded or they

high a high selectivity [31]. Ion exchange resins have limited applicability for the recovery of transition metals, due to their selectivity.

Ion exchange is often used as a remediation process to remove dissolved metals from liquids. Liquids are passed over a resin bed where ions (*i.e.*, cations and anions) in the resins and in contaminated materials are exchanged. The resins attract the metallic ions. After the resin capacity has been exhausted, resins can be regenerated for re-use. Ion exchange can remove dissolved metals and radionuclides from contaminated liquids [33]. It is used in a variety of purposes, including *ex-situ* remediation of groundwater and processing of mixed liquids wastes from storage tanks. Disadvantages of the environmental use of ion exchange resins are that oil and grease in the groundwater may clog the exchange resin and the acidity or alkalinity of the incoming water may limit ion exchange capability [33]. Additionally, oxidants in groundwater may damage the ion exchange resin and wastewater is generated during the regeneration step that requires additional treatment and disposal [33].

2.2.3 *Supported Liquid Membrane*

SLMs have even been suggested as an attractive alternative to solvent extraction. Supported liquid membrane is a new process involving extraction and stripping steps simultaneously. Supported liquid membranes (SLMs) have received considerable attention from a number of investigators because of their potential for industrial scale separation and enrichment of metal species [35]. For large scale operations, the supported liquid membrane technology is gradually replacing the conventional liquid-liquid extraction procedure due to its attractive features such as low organic to feed volume ratio, low concentration of extractants, high feed to strip ratio, low capital and operating cost, low energy requirements and a possibility to achieve high pre-concentration factors [15]. Their use in environmental applications for the cleanup of effluent streams has also received attention.

A typical SLM system consists of organic phase, a support, and two aqueous solutions (Figure 16). The organic phase is immiscible in aqueous streams and contains

the extractant, a diluent and sometimes a modifier [35]. The extractants are typically those used in solvent extraction. They can be present in trace amounts, or more often in significant amounts of up to 30% of the organic phase [35]. The extractant is diluted to a required extent and supported in a microporous hydrophobic film [36]. The supports can be used in one of several geometries. Common geometries commercially available include various flat sheets or hollow fibers. The organic solution permeates into the pores and coats the surface of the support, and the resulting thin film of organic solution forms the SLM [35].

The system is fixed in such a way that the feed circulates on the membrane face on one side and the stripping solution on the other side, allows transport of the metal ions of interest from the feed to the strip solution. The ions can be moved from lower feed to higher strip concentration solutions to concentrate the given ions to reduce the toxic aqueous liquid volumes [36]. Selective permeation is achieved when the extractant in the organic phase selectively interacts with the solute in the feed solution. The solute of interest is captured into the organic phase, and the complex diffuses through the membrane. On the stripping side of the membrane, the reaction between the solute and the extractant is reversed due to prevailing conditions. In a specific, case, the prevailing conditions favor formation of a stronger complex between a counterion in the stripping solution and the extractant [35]. The complex dissociates, and both the solute and the extractant are released; the solute passes into the solution, and the extractant remains in the SLM to repeat the cycle [35].

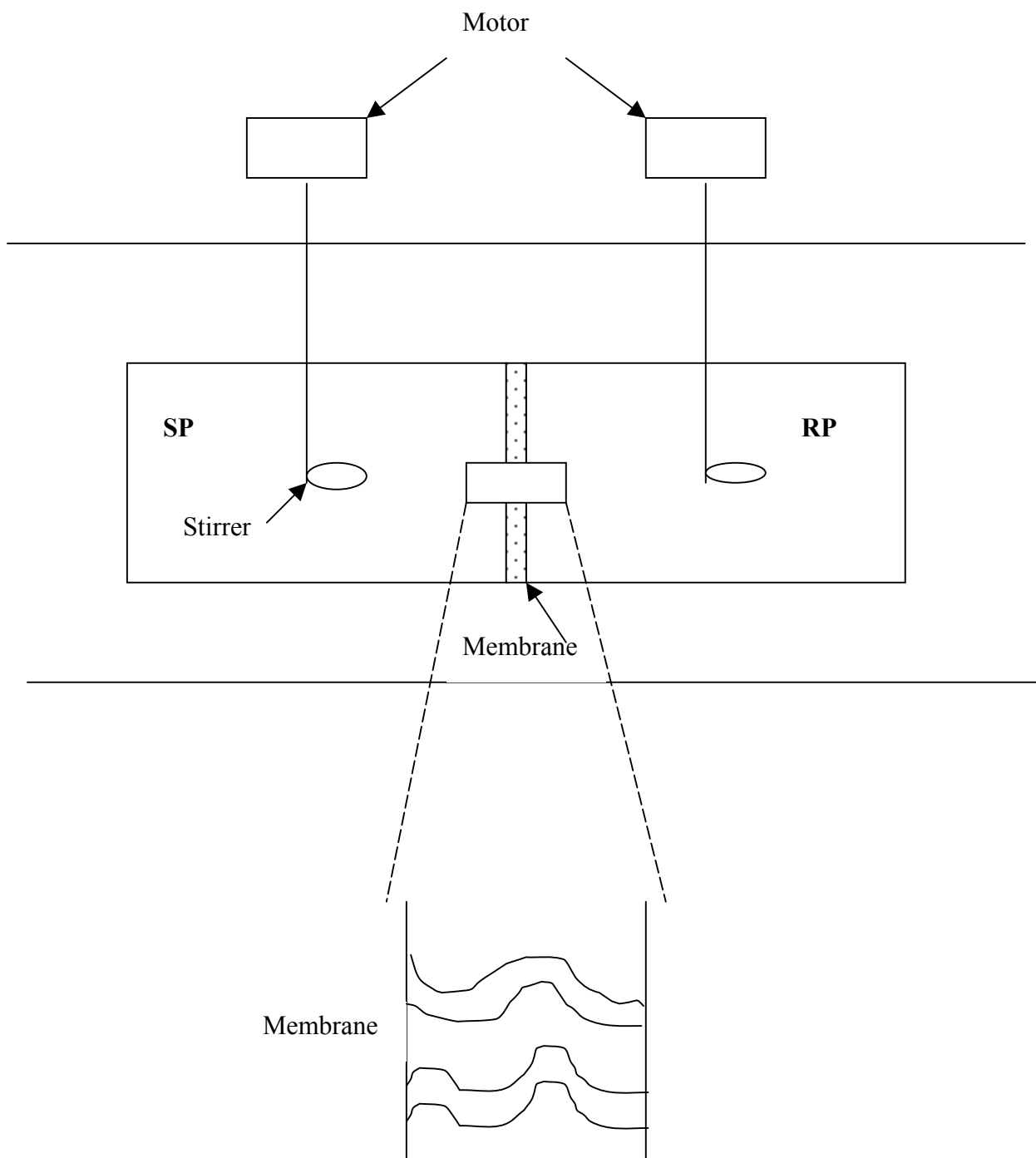


Figure 16. Typical SLM System: SP (Source Phase); RP (Receiving Phase).

2.3 *Extractant Impregnated Polymers*

Extractant impregnated polymers are an effective media for recovery and selective separation of metal ions from aqueous solutions. Extractant impregnated resins close the gap between solvent extraction and ion exchange. The bridge between solvent extraction and ion exchange was the introduction in hydrometallurgy applications of extractant impregnated membranes by Warshawsky [37]. They are a synergistic combination of sorption and reactive extraction [31]. In this method macroporous polymers adsorb liquid ion exchangers known from solvent extraction. The metals from the feed solution then react with the liquid ion exchanger on the resin and are extracted [31]. In this approach, the extractant molecules are adsorbed onto a high surface area, polymeric support to produce an extractant impregnated polymer.

Extractant impregnated polymers maintain the specificity of the metal extractants used in liquid-liquid extraction systems and avoid chemical functionalization of the polymeric support [37]. The method combines the advantages of a sorption process- the simple technique-, with those of solvent extraction- the great variety of liquid ion exchangers, which can be combined. It also offers the advantages of resin ion exchange for the processing of dilute liquors with specific properties of the solvents (or more exactly, the extractants), but also a high distribution ratio and selectivity characteristic of extractants dissolved in a liquid organic phase along with the simplicity of the equipment needs and operation characteristics of solid ion exchange technology [38].

The concept of impregnated resins was developed out of a need for ion specific resins, the availability of suitable polymeric carriers and from the deficiency in suitable methods for the chemical functionalization of polymeric carriers [34]. Two different approaches were used [39,40]: (1) physical impregnation on a selected polymeric carrier, which provides “extractant impregnated resins” and (2) copolymerization of monomer (styrene), cross linking agent (divinylbenzene=DVB) in the presence of extractant to produce Levetrel resins. The name “extractant impregnated resin” was chosen to emphasize the extractant (solvent), method (impregnation), and function (ion exchange resin) The name Levetrel® was selected by Kroebel and Meyer with emphasis on the

origin (Leverkusen) and function (extraction and elution) [34]. This work is focused on the former approach of physical impregnation.

The model of the extractant impregnated resin can be envisaged as a “liquid complexing agent dispersed homogeneously in a solid polymeric medium.” The impregnated extractant should behave as in the liquid state, but exhibit strong affinity to the matrix [34]. To obtain a material, which closely resembles the preceding model, the following requirements must be met by the extractant, the polymeric support and the impregnation method: (1) the extractant must be liquid or retained in the liquid state by the addition of diluent, (2) both the extractant and diluent should have minimal solubility in water or in the aqueous solutions employed, (3) the polymeric support should be fully expanded during the impregnation process and remain so (macroporous supports which show minimum volume variations during impregnation are preferred), and (4) the impregnation method should not destroy the properties of the extractant or the polymer[34].

The polymeric membrane, having a rigid three-dimensional structure, is most suitable to incorporate large amounts of extractants due to the high specific surface area, high mechanical strength, and rather low solvent swelling during the impregnation process. As stated previously, the attractiveness of extractant impregnated membranes lies in the possibility of selecting an existing extractant and adapting it to solve a pressing problem [38]. To produce efficient extractant impregnated resins, several impregnation methods were designed by Warshawsky, as described below:

1. *The Dry Impregnation method*- In this most widely used method, the extractant, diluted by a diluent, is contacted with the polymer, and the diluent is removed by slow evaporation under vacuum. This method is most successful in the impregnation of hydrophilic extractants such as amines, ethers, ketones, esters, *etc.*
2. *The Wet Impregnation Method*- the extractant, dissolved in a pre-calculated amount of diluent, is contacted with the polymer, until all of the liquid phase is absorbed by the polymer. The support is then immersed in aqueous metal salt

solution. After completion of the formation of the metal-extractant complex, the extractant impregnated resin is washed with water, the metal is eluted by acid, and the resin is rewashed with water. The extractant impregnated resin is then ready for application

3. *The Modifier Addition Method*- A modifier promoting water penetration into the polymer, is added. The diluent is then evaporated as in method 1. This method is a hybrid between methods 1 and 2. Sometimes, the modifier can form a part of the extractant side chains [34].

The choice of an appropriate impregnation method is essential for the stability of the system and potential application of the technique. The dry and wet surface method of impregnation are of interest in this study and will be investigated in regards to the stability of the extracting system.

2.3.1 Theory

2.3.1.a Aliquat-336

The development in the early 1960s of high molecular weight amine reagents allowed the application of solvent extraction procedures for the removal of several anions from aqueous solutions [27]. Some works utilizing amines (Alamine[®] 336, Aliquat[®] 336) for the removal of common anions have been reported: Cl⁻ and Br⁻, Ivanov and Zaitsev (1988) and Kholkin *et. al.* (1988); SO₄²⁻, Kholkin *et. al.* (1988); I⁻, Rakhman'ko *et. al.* (1988) [27]. Amines of high molecular weight have been extensively investigated for the removal of Cr(VI) [44, 27]. Additionally, economic studies have shown viability of the Cr(VI) recovery from solutions [27].

An alternate approach to conventional separation techniques such as solvent extraction is the use of hydrophobic molecules containing functional groups, such as quaternary ammonium salts. These materials loaded onto hydrophobic substrates offer several advantages, such as matrix isolation and preconcentration. Quaternary ammonium salts have been shown to be selective carriers in the extraction of heavy metals from aqueous solutions. They are able to transfer anions from an aqueous phase to

an organic phase [45]. Tetraalkylammonium salts are the most frequently used, because of their low cost and wide availability. A phase transfer agents efficacy is dependent on the lipophilicity of the cation (which affects its solubility in organic solvents and its extractive ability) and the ability of the anion, to effect ion exchange with the reagent [45]. Several works have reported the use of primary amines such as Primene JMT, secondary amines such as Adogen[®]382 and Adogen[®]283, tertiary amines such as TOA, and Alamine[®]336 [12]. Quaternary ammonium salts are reported to very effective for the removal of chromate ion from wastewater, *i.e.* TOMAC, Aliquat[®] 26, Aliquat[®] 221, and Aliquat[®] 336 [12].

Of interest in this study is the extractant Aliquat[®] 336 for the removal of Cr(VI) anions. Aliquat[®] 336 is used commercially in the solvent extraction of Cr(VI) oxyanions and consists of a mixture of high molecular weight quaternary ammonium chlorides such as methyl tri-octyl and methyl tri-decyl ammonium chloride [45]. Aliquat consists of 25 carbon atoms in the structure $\text{CH}_3(\text{CH}_2(\text{CH}_2)_7)_3\text{N}^+$ [46] (See Figure 17). Aliquat[®] 336 is classified as a phase transfer catalyst (PTC). Thus, the catalyst contains no transition metals, water-soluble components or toxic/polluting substances. PTC's are commonly used in pollution prevention, pollution treatment and the removal or destruction of impurities in waste and product streams [45].

PTC is useful primarily for performing a reaction between anions and organic substrates. PTC is needed because many anions (in the form of their salts) and neutral compounds are soluble in water and not in organic solvents, whereas the organic reactants are not usually soluble in water [45]. The catalyst acts as a shuttling agent by extracting the anion (X^-) or neutral compound from the aqueous phase into the organic reaction phase (or interfacial region) where the anion or neutral compound can freely react with the organic reactant (Q^+) already located in the organic phase (Figure 18) [45]. As larger quaternary salts are used, for example, tetraethyl, tetrapropyl, or tetrabutyl, more of the quaternary salt is partitioned into the organic phase where it can drive the reaction [45]. Increased quaternary cation size, to tetrapentyl, tetrahexyl, or tetraoctyl causes most of the quaternary salt, 95% or more, to partition into the organic phase.

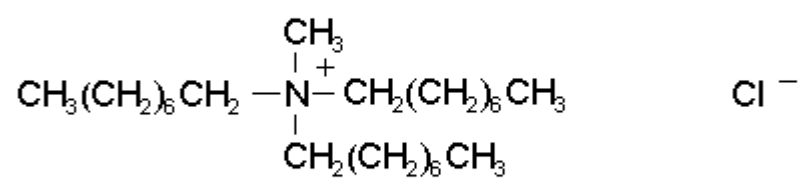


Figure 17. Aliquat[®]336.

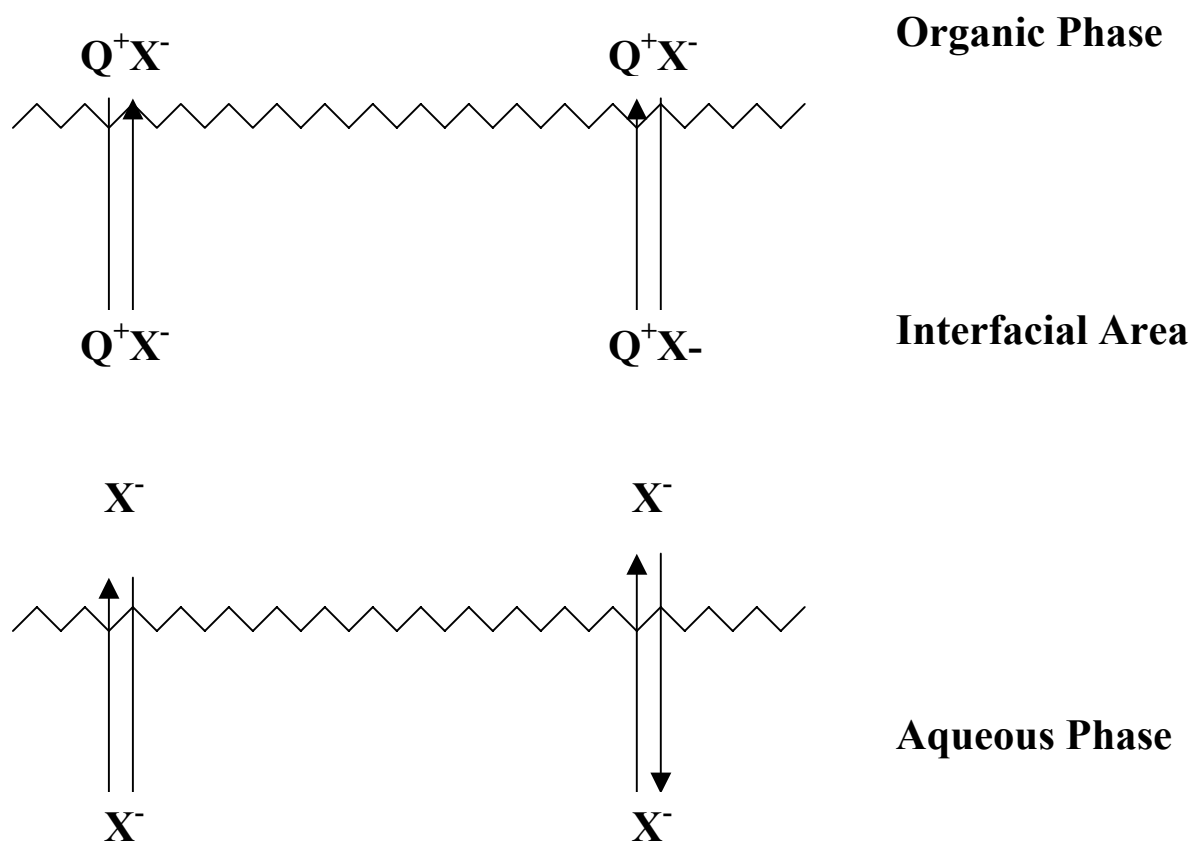
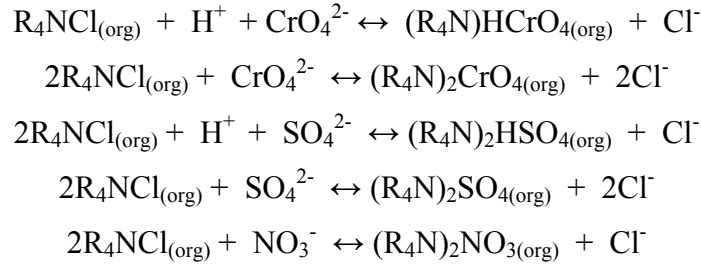


Figure 18.

Anion Transfer Across the Interface: Q^+ is quaternary ammonium salt, X^- is anion to be reacted. Reproduced from [45].

Continued increase in the chain length of tetraalkyl quaternary salt does not lead to continued increase in catalyst activity. Rather, at some point (ca. tetradecyl), catalytic activity levels off, then slowly decreases with larger and larger quaternary salt [45]. This loss of activity is due to inadequate interaction of the quaternary salt with the aqueous phase, causing the rate of anion transfer to slow, essentially resulting in a transfer-limited process due to restricted rates of anion transfer across the interface [45]. Since the catalyst is often a quaternary ammonium salt, also called the "quat" and symbolized by Q^+ , the ion pair Q^+X^- (X^- being the anion to be reacted) is a much looser ion pair than Na^+X^- . This looseness of the ion pair is another reason for enhanced reactivity.

The basic principle for the extraction of Cr(VI) by Aliquat[®] 336 is ion pair formation of Cr(VI) in acidic solution. Cr(VI) is taken up from aqueous solutions through ion pairing, and the species $(AQ)_2(CrO_4^{2-})$ is formed in the organic solution [30]. A number of equilibria that influence the extraction of Cr(VI) are involved [24]:



The above equations indicate that the extraction is affected by concentrations of chloride, nitrate, and sulfate, as well as pH [24]. These above reactions can be characterized by the equilibrium constant:

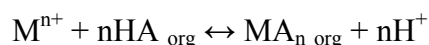
$$K_{eq} = \frac{[(AQ)_2(CrO_4^{2-})][Cl^-]^2}{[CrO_4^{2-}][AQCl]^2}$$

where AQ is Aliquat[®] 336 [30].

2.3.1.b Di(2-ethylhexyl) Phosphoric Acid (DEHPA)

A group of compounds with complexing capability for a wide range of metal cations are the organophosphates, which have been widely utilized as conventional extractants in liquid-liquid extraction procedures for both transition and rare earth elements [47]. Organophosphorus solvents are one of the largest family of metal extractants used in hydrometallurgical applications [48]. Di(2-ethylhexyl) Phosphoric Acid (DEHPA), is an acidic metal extractant, which falls in the category of organophosphorus solvents. This class of extractants includes esters of orthophosphoric, phosphonic and phosphinic acids, and similar compounds containing polyfunctional groups (Figure 19). The active group of the organophosphorus acids, P(O)OH, is responsible for their extractive properties. Of these reagents alkylphosphoric acids have proved to be the most versatile, especially DEHPA. DEHPA is a useful solvent for concentrating and purifying valuable metal solutions including uranium, cobalt and nickel, rare earths, and vanadium [49]. Some of particular advantages of the use of DEHPA in solvent extraction are its chemical stability, good kinetics of extraction, good loading and stripping characteristics, low solubility in the aqueous phase, versatility in the extraction of many metals, and its availability in commercial quantities.

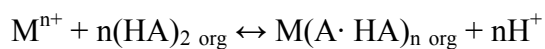
The mechanism and kinetics of metal ion transport in a liquid membrane system containing DEHPA as the extractant has been studied in some detail previously [50, 51, 52]. Studies on metal extractions using DEHPA as the extractant have indicated two extreme situations depending on the metal ion concentration. At low metal loading (tracer levels), metal extraction is considered to occur according to the equation:



which can be characterized by the equilibrium constant [48]:

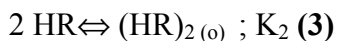
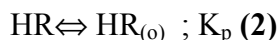
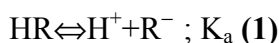
$$K_{eq} = \frac{[MA][H^{+}]^n}{[M^{n+}][HA]^n}$$

whereas at higher metal loading the available evidence supports the view that extraction occurs according to:



The mechanism of cation exchange by DEHPA is the hydrated metal cation reacts with the extractant molecules at the aqueous/membrane interface to first form a neutral species. The neutral species formed then replaces its coordinated water molecules with free DEHPA molecules (HA) to form the final species, which is soluble in the membrane $\text{Cr}^{3+} + 2(\text{RO})_2\text{P}(\text{O})\text{OH} \leftrightarrow [(\text{RO})_2\text{P}(\text{O})\text{O}]_3\text{Cr} + 3\text{H}^+$. DEHPA is monobasic in nature and thus releases one hydrogen ion for every molecule, which combines with the metal. The number of molecules of extractant involved in the formation of an extracted species depends on the oxidation state. Thus, in the extraction of Cr(III) by DEHPA, three hydrogen ions are released for every DEHPA molecule.

Jerabek *et. al.* (1996) studied the relationship between the impregnation process and polymeric support of DEHPA and found that DEHPA gradually fills the pore space during impregnation from the smallest pores up to larger pores. This process was most likely connected with the strong cohesion force observed between DEHPA molecules. They also found that the sorbed DEHPA fills almost all its porous system [53]. It is well known that acidic organophosphorus compounds such as DEHPA mainly exist as dimers in nonpolar or low polar organic solvents due to strong intermolecular hydrogen-bonding [38]. In the aqueous phase, DEHPA exists mainly as monomers because the intermolecular hydrogen-bonding between the acids is destroyed by preferential hydrogen-bonding with water [38]. Hence, for the systems of interest:



where the (o) refers to the resin phase, K_a is the acid dissociation constant, K_p is the partition coefficient, and K_2 is the dimerization constant.

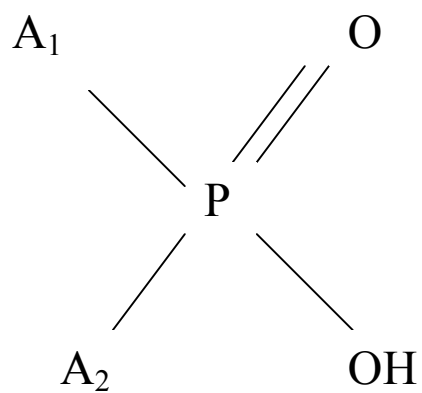


Figure 19. Organophosphorus Acids Derivatives: $A_1 =$ or $\neq A_2$

$A = \text{OH}, \text{OR}, \text{OAr}, \text{R}, \text{Ar}$

Juang *et. al.* found that the equilibrium constants for distribution of DEHPA between the macroporous polymer, XAD-2, and the aqueous phase were $\log K_p=4.72$, $\log K_2=-0.52$, and $pK_a=2.90$ at 298 K. In comparison with the corresponding constants obtained in extractant impregnated membrane systems and in the bulk organic solvents, as expected, K_a is equivalent. A requirement of the extractant in the impregnation of membranes is that it should display the same extractive capabilities in the resin as it does in bulk organic solvents, hence K_a should be equivalent to that observed in bulk.

On the other hand, K_p is significantly greater in extractant impregnated polymer systems, indicating that the distribution of DEHPA is shifted more toward the resin phase, due to the interaction of DEHPA with the resins. Moreover, K_2 is much smaller in SIR systems; *i.e.*, DEHPA molecules mainly exist as monomers rather than dimers in the resin phase.

2.4 Summary

Through the need for specific systems, new ion exchange resins, solid adsorbents and metal extractants used in solvent extraction processes have been developed for different applications. In this approach, the extractant molecules are adsorbed onto a high surface area, polymeric support to produce an extractant impregnated polymer. Extractant impregnated polymers maintain the specificity of the metal extractants used in liquid-liquid extraction systems and avoid chemical functionalization of the polymeric support. The principles of solvent extraction, ion exchange and supported liquid membranes all form the basis for extractant impregnated membranes. Solvent extraction has received a great deal of attention, especially for the treatment of solutions with high relative metal concentrations. It is a significant method based on the solubility of an analyte between two immiscible liquids. Ion exchange involves functional groups of organic polymers, which bind cations and anions. In the case of supported liquid membranes, the inclusion of a relatively small amount of extractant in the form of a film barrier between two phases can be accomplished.

The application of extractant impregnated membrane technology offers considerable advantages over solvent extraction, ion exchange and supported liquid membranes. The major drawback of solvent extraction is the dispersion of the solvent, which has both environmental and economic implications. Ion exchange has the disadvantages of a limited range of possible applications, compared with reactive extraction. The choice of a suitable ion exchange resin is also often difficult, since the resins can be either high loaded or they have a high selectivity. Supported liquid membranes hold the promise of high performance with a minimal amount of extractant. This presents an advantage over solvent extraction. One weakness of supported liquid membranes is the loss of extractant to the aqueous phase, which has a profound effect on the lifetime of the system.

The extractants commonly used in extractant impregnated membranes are those generally employed in solvent extraction. The quaternary ammonium salt, Aliquat[®] 336 has been extensively used in solvent extraction and reported to be a very efficient extractant in the removal of Cr(VI) anions. The acidic organophosphorus extractant, DEHPA, has been widely studied and has been shown to be an effective extractant for transition metals and lanthanides.

The increasing concern towards the removal of transition metal ions from industrial wastewaters and groundwater requires the development of advanced separation systems. The simultaneous oxidation of Cr(III) to Cr(VI) and reduction of Cr(VI) to Cr(III) and the interconversion and degradation processes encompassing chromium chemistry make sampling difficult. Often, laboratory measurements do not reflect the concentrations of species taken at the point of collection. Majority of the work on Cr speciation generally demonstrate high sensitivity and selectivity but there is an urgent need for reproducible sampling and minimal sample preparation, good separation, and metal species preservation. This work centers on the application of extractant impregnated polymers for the *in-situ* sampling, separation/removal, and stabilization of chromium species.

Chapter 3

3. Experimental Methods and Procedures for Analytical Measurements

3.1 Reagents

Plastic and glassware were soaked in 1:1 HNO₃ for two days and thoroughly rinsed with high purity water (18 MΩ) before use. Nitric acid was supplied by Fisher Scientific and purified by a laboratory constructed sub-boiled distillation still [18]. Dilutions were prepared using 18 MΩ distilled water (Millipore-Q). All other reagents were prepared from analytical grade chemicals. Tricaprylmethylammonium chloride (Aliquat-336) and di-(2-ethylhexyl) phosphoric acid (DEHPA) were obtained from Sigma-Aldrich (St. Louis, MO). The organic solvent for dissolution, petroleum ether Sigma-Aldrich (St. Louis, MO) was used without further purification. Standard solutions of Cr(III) and Cr(VI) were prepared by appropriate dilutions of stock solutions of potassium dichromate and chromic nitrate from Sigma-Aldrich (St. Louis, MO). Metal ion solutions were prepared from 1000 mg/L stock solutions of Fe³⁺, Cu²⁺, Cd²⁺, Co²⁺, Al³⁺, and Zn²⁺ from Ultra Scientific (North Kingstown, RI). 1,5-diphenylcarbohydrazide was obtained from Aldrich (St. Louis, MO) and prepared according to SW-846 Method 7196A. Sulfuric acid was obtained from VWR (W. Chester, PA). Strip solutions were prepared by appropriate dilutions of concentrated nitric acid supplied by Fischer (Fairlawn, NJ) and sodium hydroxide mono-hydrate (Sigma-Aldrich, St. Louis, MO).

3.2 Materials & Apparatus

The polymeric substrates were obtained from Whatman (Clifton, NJ) and Pall Gelman (Ann Arbor, MI). The Whatman[®] PP membrane is polypropylene and the Versapor[®] 450 membrane is an acrylic non-woven copolymer. These polymeric membranes are inert, high purity polymeric supports, which can be used with all aqueous solutions and many organic solvents (Dow Chemical). The column was modified from a commercial flow cell made of cast plastic available (3.0" o.d., 2.5" i.d., 8" long) from Soil Measurement Systems (Tucson, AZ). Modification of the flow cell is described further in the Column Design section. PVC tubing (3/16"x 5/16") tubing was used to

connect the pump, column, and source solution. A VWR variable speed pump was used to pass the aqueous source solutions through the flow cell. Acid washed seasand from Fischer Scientific (Fairlawn, NJ) was used. The entrance and exit membranes were nylon mesh membranes supplied by Soil Measurement Systems. The nylon mesh membranes are porous and hydrophilic with a diameter of 30 μm and thickness of 60 μm . Nylon mesh is used in the column to hold the sand inside the column during flow studies. Aluminum perforated disks supplied by Soil Measurement Systems were used to disperse the aqueous media. Versapor-450 membranes were used as spacers between the aluminum perforated disks and seasand. A Fisher Scientific Accumet[®] AR10 pH meter (Fairlawn, NJ) was used for pH measurements.

3.3 *Extraction Methods*

In the study of the extraction efficiency of the prepared extractant impregnated membranes, two extraction methods were investigated: batch and column. The batch methods of extraction were conducted to determine the optimal conditions (*i.e.* choice of extractant/stripping agent, extractant/stripping concentration, etc.) to obtain maximum efficiency. Batch extractions were first conducted in equilibrium (liquid-liquid extraction) to observe the extraction efficiency of the system (equal volumes of aqueous and organic phases) prior to impregnation of the organic solvent system on polymeric supports. Once the performance of the batch extraction system was investigated in equilibrium, batch experiments then transitioned into the study of the impregnated polymeric membranes in contact with the aqueous phase containing the ion(s) of interest. Batch experiments consisting of the impregnated membranes and aqueous phase were conducted by simple immersion of the impregnated membranes into the aqueous phase containing the ion(s) of interest. The extraction efficiency of the impregnated membranes was noted and subsequently compared to the extraction efficiency column experiments.

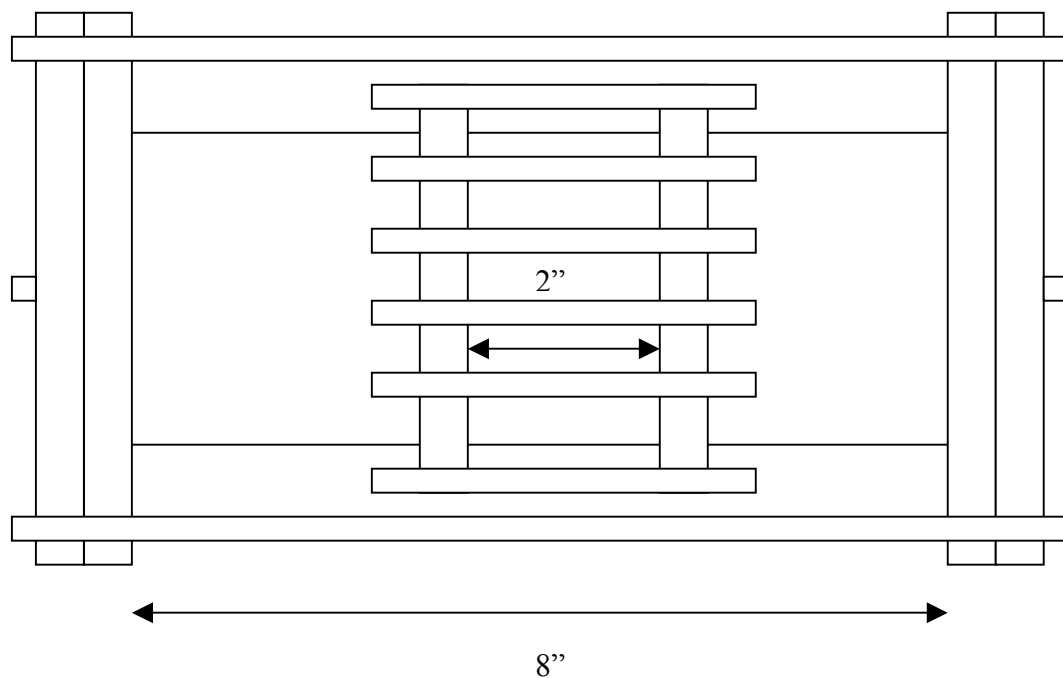
The results obtained from batch investigations gave insight into the performance of the impregnated membranes when incorporated into a sampling system such as columns. The column studies were conducted to observe the performance of the sampling system under conditions simulating their potential application, which is a sampling

device capable of *in-situ* separation, preservation/stabilization of chromium species at the source of contaminated sites. Column studies give a more accurate representation of the performance of the sampling system under simulated environmental conditions. The experiments were conducted using the apparatus described below.

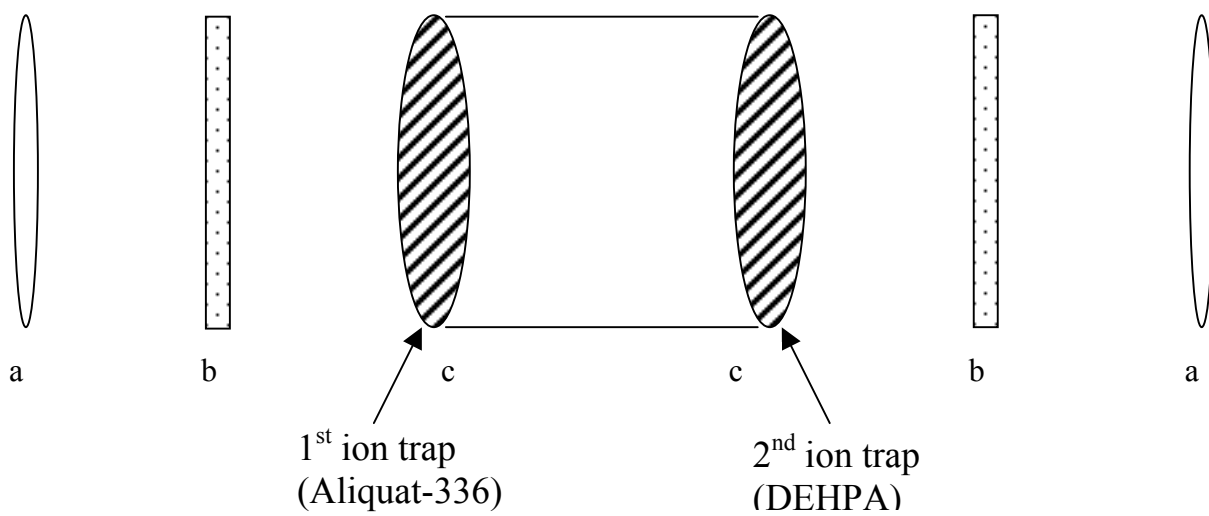
3.4 *Experimental Design and Assembly*

A schematic for the column design is shown in Figure 20a. The column consists of a tube with two removable end-plate assemblies mounted on both ends. The top and bottom end-plate assemblies are held together with 3 rods. Each end-plate assembly consists of two parts: a round doughnut shaped part that contains an o-ring, and that slides over the end of the column, and a flat round plate which holds a perforated aluminum support disc. There is a flat ring between the two plates, as well as a porous nylon membrane. This 8" flow cell was cut to provide a 2" removable section in the middle of the cell. This 2" midsection housed the extractant impregnated membranes (selective ion trap).

The selective ion trap was first removed from the flow cell and extractant impregnated membranes were placed into this assembly as illustrated in Figure 20b. Gaskets were placed at the ends of the trap to prevent leakage. The extractant impregnated membranes were then placed at the ends followed by an additional perforated aluminum disk and then a spacer to prevent contact between the seasand and perforated aluminum disks. The assembled trap was then incorporated back into the flow cell through the use of flanges held together with 6 rods. Once the trap is placed back into



(A)



(B)

Figure 20. (A) Horizontal View of Column Design and (B) Exploded View: (a) extractant impregnated membranes (b) aluminum perforated disk (c) spacer.

the cell the entire column is tightly held using 3 rods on the top and bottom end-plate assemblies.

The experimental setup for the column experiments is illustrated in Figure 21. Acid washed seasand was placed into the end sections of the column and the selective ion trap was interposed in the middle. The column was oriented vertically, and the source solution was introduced at the top of the flow cell. The source solution used was a synthetic groundwater solution (SGW), simulating the composition of groundwater. The composition of the SGW is reported in Table 9. This SGW was stored in a 1000 mL polyethylene storage bottle with a screw cap. This screw cap was modified to allow the source to be pumped directly from the storage bottle. A hole was drilled to accommodate the PVC tubing, which was connected to the variable speed pump. The flow cell was operated under saturated conditions (no vacuum was needed) at 1 mL/min and the extract was collected from the bottom of the flow cell. After 24 hrs, the extract was obtained analyzed by UV-VIS/ICP-AES. The extract was taken every 24 hrs until no further decrease in Cr(VI)/(III) concentration was observed (*i.e.* no further increase in extraction efficiency). The extractant impregnated membranes were then withdrawn from the flow cell and stripped of the analyte of interest with the appropriate eluent (HNO₃/NaOH).

3.5 *Instrumentation*

3.5.1 *UV-VIS Spectrometry*

Cr(VI) was determined using a Perkin-Elmer Lambda 4B UV-VIS. SW-846 method 7196 was employed which is a colorimetric determination of Cr(VI) using 1,5-diphenylcarbohyrazide (DPC) measured at 540 nm. In all determinations recommended parameters were used.

3.5.2 *Inductively Coupled Plasma Atomic Emission Spectrometry*

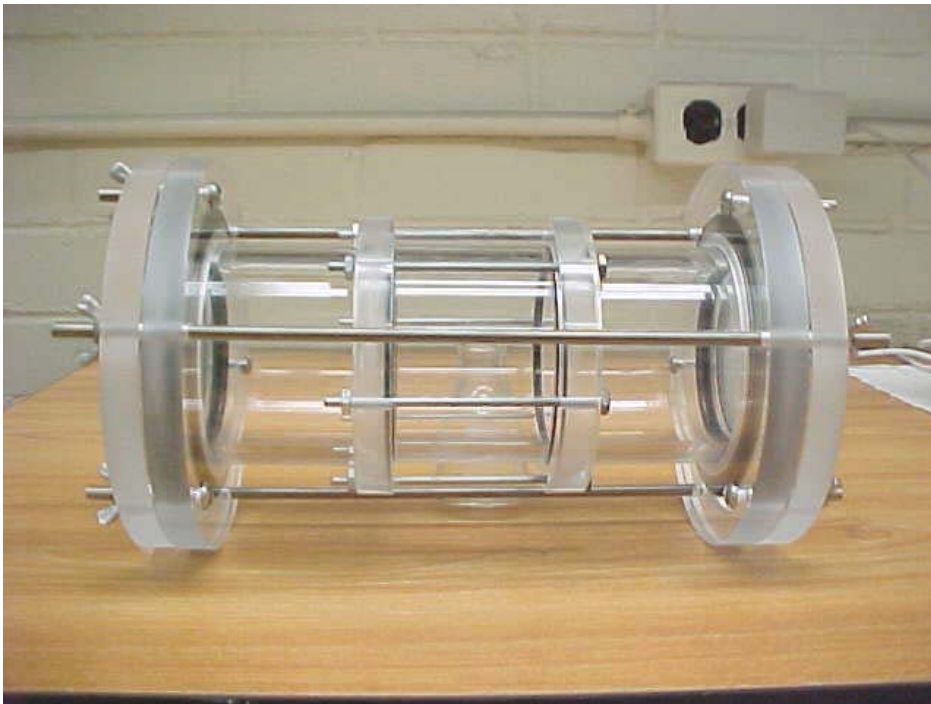
An Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES) Perkin Elmer ICP 6000 was used in total metal analysis of chromium species. The



Figure 21. Experimental Setup.



(a)



(b)

Figure 22. Column (a) entrance/exit view (b) side-view.

Table 9. Composition of Synthetic Groundwater.

Constituent	Molarity
Calcium	0.012
Magnesium	0.0062
Sodium	0.017
Silicon	0.0009
Chloride	0.0016
Sulfate	0.017
Nitrate	0.030
Chromium(III)	0.00094
Chromium (VI)	0.00094
Sum of Molarities	0.087

intensity of the atomic line at 267.7 nm was monitored. In all determinations recommended parameters were used.

3.5.3 *Surface Analysis*

Topographical images of the sample surfaces was accomplished using Scanning Electron Microscopy (SEM) model ISI-SX-40. The extractant impregnated membranes were gold coated to obtain a conducting surface for the SEM images. The elemental composition of sample surfaces was accomplished using X-ray Photoelectron Spectroscopy (XPS) Perkin Elmer Model 04-500 equipped with a Mg/Al anode. No sample preparation was necessary in the XPS surface analysis of the extractant impregnated membranes. One scan of a 1 mm x 3 mm sample size was taken of each sample.

3.6 *Experimental Procedure*

3.6.1 *Preparation of Organic Solvent System*

The composition of the organic solvent system is important in that the diluent and extractant are required to have negligible solubility in the aqueous phase. Additionally, the extractant must be retained in the liquid state. The solvent system is composed of the organic solvent petroleum ether and the extractant Aliquat-336 or DEHPA for Cr(VI) and Cr(III) species, respectively. The amount of extractant dissolved in the organic solvent was varied in amounts of approximately 0.5% to 30% by volume of the organic solvent system. A modifier, 5 v/v% isodecanol, was added to avoid formation of a third phase.

3.6.2 *Preparation of Extractant Impregnated Membrane*

It is essential to the stability and the extractive properties of the technique that the extractant impregnated membrane not destroy the properties of the extractant or the polymer. Once the extractant is impregnated, it must maintain the properties of the free extractant. This approach allows simple preparation of impregnated polymers with the appropriate selective extractant. Once the extractant is dissolved in the organic solvent system, the polymeric support is contacted with the solution by immersing (dip-coating)

the substrate into the prepared solution. The organic solvent is removed by simple evaporation at ambient conditions. Thus, providing a passively coated thin layer film of the extractant on the surface.

3.6.3 *Stability of Chromium Standard Solutions*

An important task was the validation of the integrity of chromium standard solutions. Interconversion and degradation of chromium standard solutions must be negligible to assure reproducibility and accuracy of the technique. The influence of pH, light, time, storage container, and temperature on the stability of prepared standards of chromium (III) and chromium (VI) were investigated. To avoid alteration of the oxidation state during sampling and storage these parameters were studied in an effort to ensure that the technique yields an accurate representation of the sample taken at the point of collection.

3.6.4 *Storage of Chromium Solutions*

Due to the problematic storage of chromium (III)/(VI) samples which originates from interconversion and degradation processes, the stability of chromium (III)/(VI) solutions was studied and the best protocol for maintaining the integrity of the samples was observed. Chromium standard solutions of 50 ppm concentration were stored in polyethylene bottles, amber glass, and clear glass flasks. Solutions were then stored at room temperature and refrigerated at 4°C. Storage at room temperature was performed to assess the stability of chromium species when stored at natural pH and room temperature. These results were compared to those of the refrigerated solutions in an effort to observe any speciation changes.

3.6.5 *Equilibrium Investigations (Aliquat-336)*

Before membrane studies could be performed, it is important that equilibrium investigations be conducted to determine the optimal operating conditions in which to carry out the membrane and kinetic studies. In equilibrium investigations of the free extractant, equal volumes of the aqueous solution containing the metal ion of interest and an organic solution containing Aliquat-336 were shaken for an hour. The two phases

were completely separated and the metal concentration was determined in the aqueous phase and the percent extracted calculated. The stripping experiments were carried out by shaking equal volumes of the organic solution loaded with the maximum extracted concentration of the investigated metal and aqueous solutions of HNO_3 . After phase separation, the concentration of stripped metal in the aqueous phase was determined and the percent stripped was calculated.

3.6.6 Effect of Extractant Concentration

The efficiency of Cr(VI)/(III) extraction may be highly dependent on the concentration of extractant in the organic solvent system. High concentrations of extractant may result in no further increase in extraction efficiency after some point and too small a concentration may result in incomplete extraction. Therefore, the dependence of extraction efficiency on extractant concentration was studied. The concentration of Aliquat-336 or DEHPA dissolved in petroleum ether was varied (0.5 v/v%-10 v/v% Aliquat and 1 v/v% - 40v/v% DEHPA) and an optimal extractant concentration was determined and used for further experiments.

3.6.7 Effect of Stripping Agent Concentration

The choice of stripping agent is essential in the quantitative recovery of analyte. An inappropriate choice of stripping agent could result in incomplete recovery or alteration of chromium species during stripping. Therefore, the stripping efficiency was observed for HNO_3 and NaOH for Cr(III) and Cr(VI) species, respectively. The concentration of stripping agent is also important in an attempt to obtain complete recovery and maintain the original speciation state of the sample. Therefore, the concentration of the strip solution (HNO_3/NaOH) was varied to observe the optimal strip concentration necessary for extraction of chromium species. Special care was taken to observe the optimal stripping agent pH to assure preservation of Cr (III)/(VI) anionic species. The optimum stripping solution concentration determined in this set of experiments was used in further investigations.

3.6.8 *Extraction of Cr (VI) using Extractant Impregnated Membrane*

Optimal conditions of extractant concentration and choice of stripping agent and concentration were determined from equilibrium investigations, and these conditions were then applied to membrane studies. The impregnated membrane was prepared as described previously. The impregnated membrane was submersed into an aqueous solution containing 50 ppm chromium (VI). Each hour, an aliquot of the aqueous solution was taken for chromium analysis. After no further decrease in chromium concentration was observed (*i.e.* no further increase in extraction efficiency within a 24hr period), the extracted chromium was stripped from the membrane using the appropriate stripping agent (HNO_3 for Cr(III) or NaOH for Cr(VI) and the concentration of stripped metal was determined by UV-VIS and the percent stripped was calculated.

3.6.9 *Extraction of Cr (III) using Extractant Impregnated Membrane*

The impregnated membrane was submersed into an aqueous solution containing 50 ppm chromium (III). Each hour, an aliquot of the aqueous solution was taken for chromium analysis. After no further decrease in chromium concentration was observed (*i.e.* no further increase in extraction efficiency within a 24hr period), the extracted chromium was stripped from the membrane using the appropriate stripping agent (HNO_3 or NaOH) and the concentration of stripped metal was determined by ICP-AES and the percent stripped was calculated.

3.6.10 *Effect of Source Concentration*

Extraction efficiency may be dependent upon the concentration of analyte in the source phase. Extraction efficiency may vary at high/low concentrations of analyte, which in turn may limit the application of the technique. Therefore, the influence of the source concentration (*i.e.* the solution containing the metal ion) on extraction efficiency was studied to observe the optimal source concentration necessary to achieve optimum extraction of chromium species.

3.6.11 Influence of Source pH

Chromium speciation is highly variable upon pH [16]. This change in speciation attributed to pH may have a drastic effect on the extraction efficiency of the system. The optimal pH conditions of the extraction technique may not reflect the natural pH of chromium species found in environmental matrices. Therefore, the influence of pH on extraction efficiency was investigated. The pH of Cr(III) and Cr(VI) aqueous solutions was varied from a pH of 2-11 using NaOH and 10 v/v% H₂SO₄. Extractant impregnated membranes were immersed and equilibrated with the prepared aqueous solutions containing the metal ion of interest. Every 24 hrs, an aliquot of the aqueous solution was taken for chromium analysis. The optimum pH range was noted and used in further experiments.

3.6.12 Effect of Competitive Anions on Cr (VI) Extraction Efficiency

Extractants often used in solvent and membrane extraction techniques rarely exhibit complete selectivity for one solute over all others in solution. In the presence of competitive anions, chromium (VI) may show variable extraction efficiency. It is important to study the effect of competitive anions on Cr(VI) extraction due to their ubiquitous presence in environmental matrices. In this set of experiments, the extraction of Cr (VI) was investigated in the presence of three common interfering anions (NO₃⁻, SO₄²⁻, Cl⁻). Three solutions of sodium salts (NaNO₃, Na₂SO₄, and NaCl) were prepared to maintain a constant ionic strength of 0.1 M. Aliquat-336 impregnated membranes were immersed into the prepared aqueous solutions containing 50 ppm of Cr(VI). An aliquot of the aqueous solution was taken for chromium analysis after a 24 hr interval. The extracted chromium was stripped from the membrane using the appropriate stripping agent and the concentration of stripped metal was determined by UV-VIS and the percent stripped was calculated.

3.6.13 Effect of Competitive Cations on Cr (III) Extraction Efficiency

Chromium (III) will commonly be found in close association with other cation constituents in environmental matrices many of which exhibit similar chemistry to Cr(III). As a result, Cr(III) extraction efficiency may be highly dependent upon other

cationic constituents in solution. Therefore, the extraction of Cr (III) was investigated in the presence of the interfering cations (Fe^{3+} , Ni^{2+} , Al^{3+} , Mg^{2+}). Metal ion solutions at a concentration of 50 ppm were prepared from 1000 mg/L stock solutions. DEHPA impregnated membranes were immersed into the prepared aqueous solutions containing Cr(III). An aliquot of the aqueous solution was taken for chromium analysis after a 24 hr interval. The extracted chromium was stripped from the membrane using the appropriate stripping agent and the concentration of recovered metal was determined by ICP-AES and the percent stripped was calculated.

3.6.14 Membrane Lifetime and Stability

The stability of the system was the next area of study. This area was one of concern due to the fact that stability of the impregnated membranes may vary when used during equilibrium experiments versus dynamic experiments in which the flow is continuously pumped through the impregnated membrane. Membrane instability may be dependent upon many factors including solubility of the extractant in the aqueous phase, flow, adherence to the polymeric support, *etc.* Extraction efficiency of the system would be highly dependent upon the stability of the impregnated membrane under different conditions. Therefore, the stability of the extractant impregnated membranes was studied in order to assess the applicability and lifetime of the system. Lifetime and stability of the system was determined through use of the weighing method [54]. Loss of the extractant from the membrane to the aqueous solution was measured as a measure of weight loss difference between the freshly prepared impregnated membrane and the decayed membrane. The amount of extractant lost within the membrane pores and surface was obtained by weighing the freshly prepared impregnated membrane and decayed membrane on an analytical balance and subtracting the former from the latter. Extractant loss from the membrane to the aqueous phase was studied as a function of shear forces induced by flow and extractant loss to the aqueous phase under equilibrium conditions.

Chapter 4

4. Results & Discussion

4.1 *Stability of Chromium Standard Solutions*

Due to the fact that Cr(VI) is an oxidizing agent, care must be taken in the storage of samples and standard solutions. Sampling and preservation procedures often involve changing sample pH. Changes in pH may result in an alteration of relative concentration of oxidation states. As a result, the stability of chromium (III)/(VI) samples is a most important criterion for the accurate assessment of the analytical methods due to the problematic storage of chromium samples originating from interconversion and degradation processes. The first task was to validate the integrity of the chromium standard solutions. Interconversion and degradation of chromium standard solutions must be negligible to assure reproducibility and accuracy of the technique. The influence of pH, light, time, storage container, and temperature on the stability of prepared standards of chromium (III) and chromium (VI) were investigated. In order to avoid alteration of the oxidation state during sampling and storage these parameters were studied in an effort to ensure that the technique yields an accurate representation of the sample taken at the point of collection.

Results from this study indicate that optimal storage of chromium solutions be refrigerated storage at 4°C in clear polyethylene bottles to prevent interconversion or alteration in oxidation state of the samples (Figure 23). The results obtained are for Cr(VI) and Cr(III) standard solutions in reagent water. Storage of environmental samples would show a different behavior, due to the presence of organic matter and colloidal material, which would have a negative effect on the storage stability of different chromium species [24].

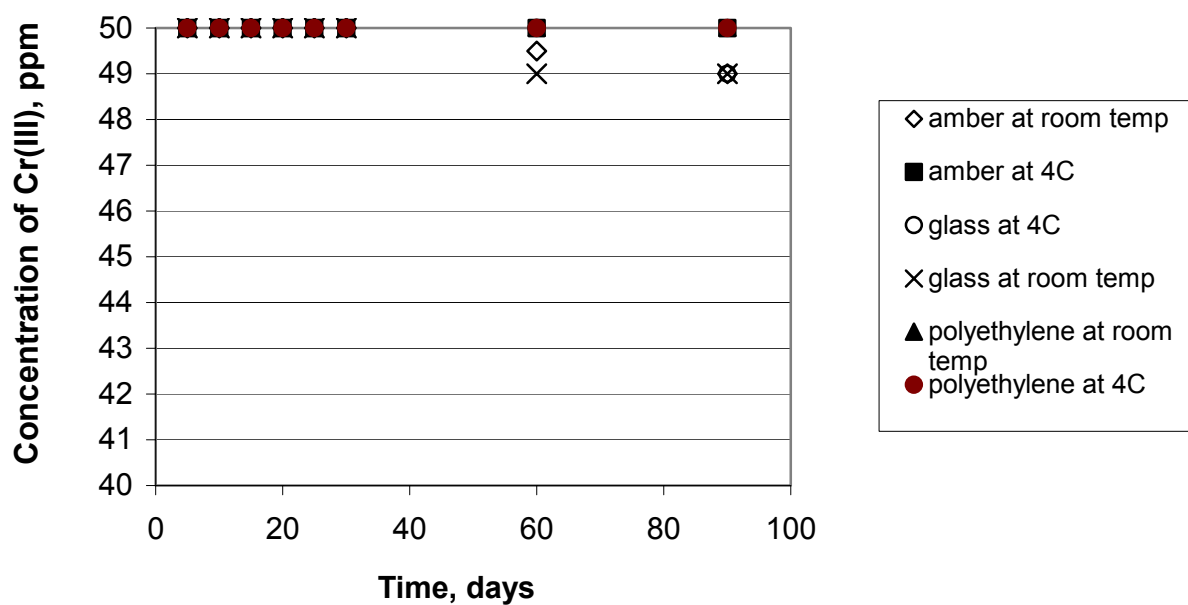
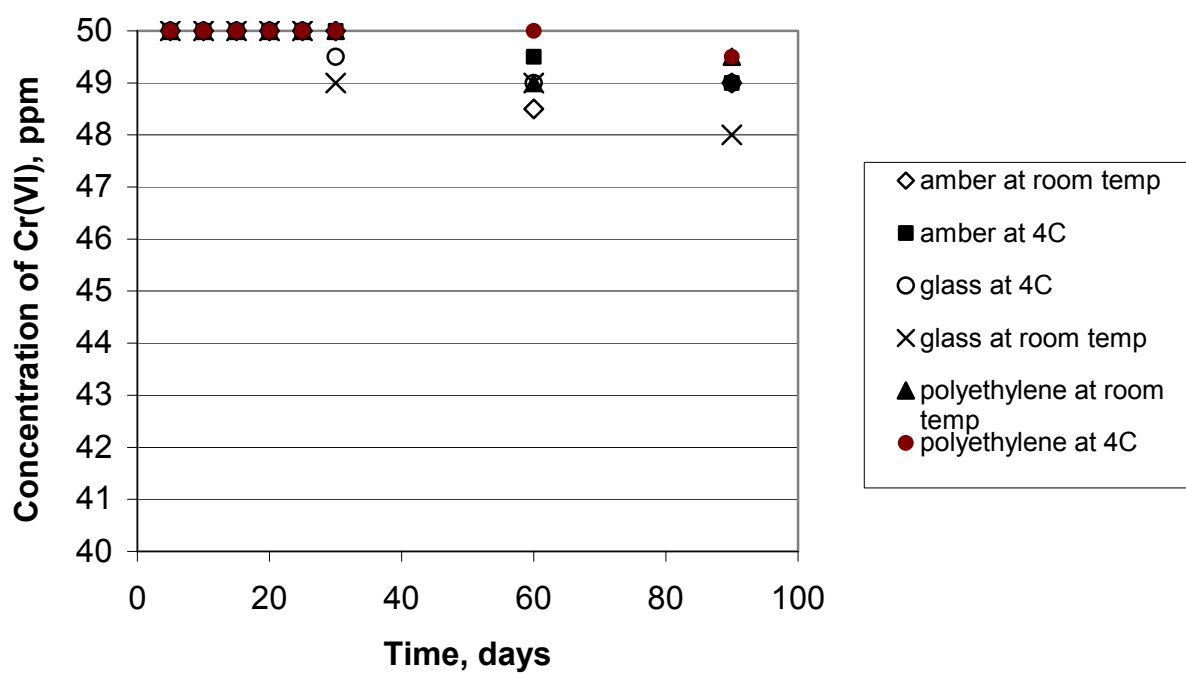


Figure 23. Stability of Chromium Standard Solutions: source concentration 50 ppm Cr(VI)/Cr(III); source pH=3.5.

4.2 Batch Investigations (Liquid-liquid Extraction)

4.2.1 Effect of Extractant Concentration

It is important that equilibrium investigations be conducted in order to determine the optimal operating conditions in which to carry out the membrane and kinetic studies before membrane studies can be performed. The efficiency of Cr(VI)/(III) extraction has been shown to be highly dependent on the concentration of extractant in the organic solvent system. Figure 24 shows the effect of extractant concentration on extraction efficiency of *Aliquat-336* and *DEHPA* for Cr(VI) and Cr (III), respectively. The concentration of *Aliquat-336* or *DEHPA* dissolved in petroleum ether was varied and an optimal extractant concentration was determined and was used for further experiments. There is an observable increase in extraction efficiency with extractant concentration of *Aliquat-336* up until 1v/v% after which it drops. The decrease in extraction efficiency is attributed to the occurrence of third phase formation which prevents complete extraction of Cr(VI) through incomplete separation. Aggregation of the extractant in the organic phase may also contribute to the decrease in extraction efficiency:

$R_4N^+ X^- \leftrightarrow (R_4N^+ X^-) \leftrightarrow (R_4N^+ X^-)_n$. Similar results were obtained for supported liquid membrane studies for chromium with Aliquat [15].

There is also an increase in extraction efficiency with extractant concentration of *DEHPA* up until 30v/v% after which it wanes. The decrease in extraction efficiency is also attributed to the increase in viscosity of the organic phase at higher extractant concentration [47]. Additionally, a decrease in extraction efficiency with extractant concentration of *DEHPA* could be due to the formation of higher association complexes that are not available for extraction by *DEHPA* [47].

4.2.2 Effect of Modifier on Cr(VI) Extraction

Insufficient extraction of Cr(VI) species during equilibrium investigations were attributed to the presence of a 3rd phase in the extraction of Cr(VI) with Aliquat. As a result, the influence of the addition of isodecanol as modifier on extractant efficiency was investigated. Adding 5 v/v% isodecanol as modifier to the organic phase avoided the

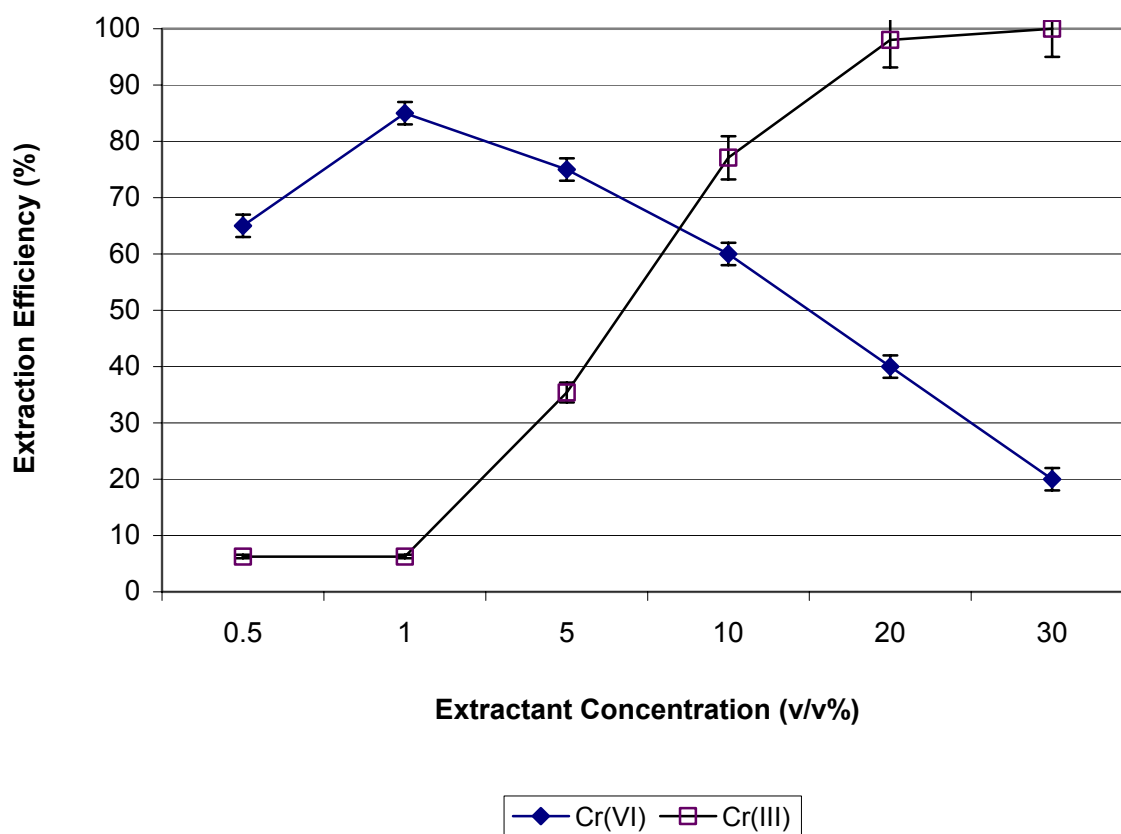


Figure 24.

Effect of Extractant Concentration (Liquid-liquid extraction): 1 v/v% Aliquat-336, 30 v/v% DEHPA; source concentration 50 ppm Cr(III)/Cr(VI); source pH 3.5.

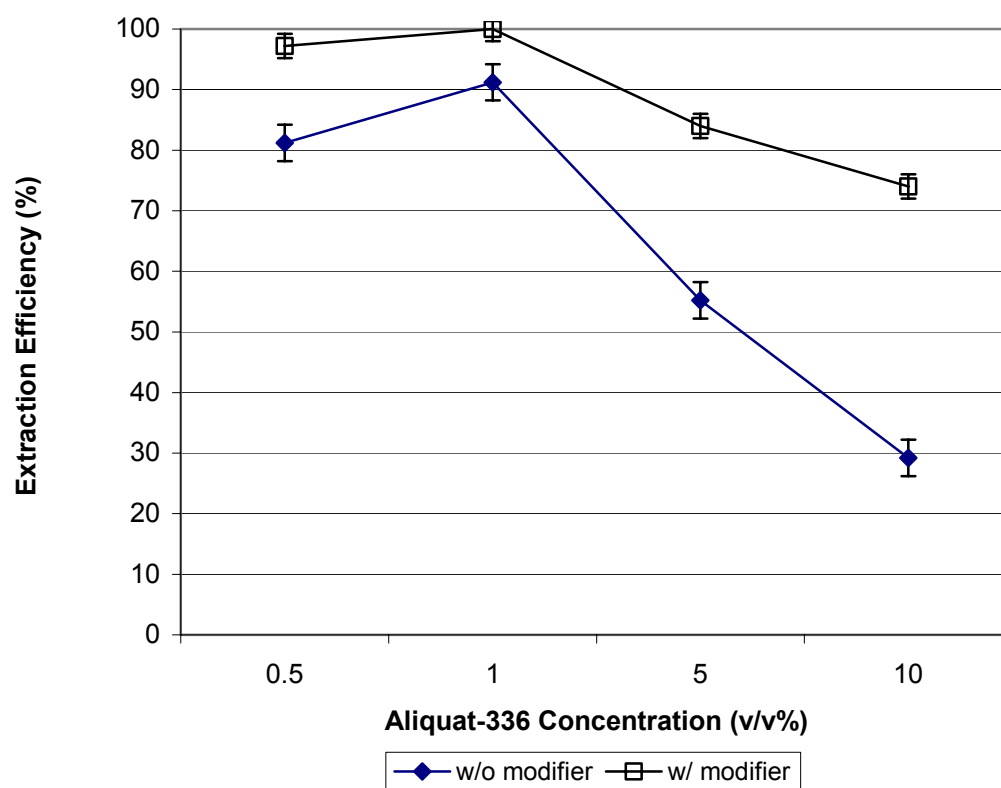


Figure 25.

Effect of Modifier on Cr(VI) Extraction (Liquid-liquid extraction): 1 v/v% Aliquat-336; modifier= 5% isodecanol; source composition 50 ppm Cr(VI); source pH=3.2.

formation of third phase as the interphase between the aqueous and organic phases that could inhibit extraction. This resulted in an increased solubility of extracted complexes in organic phase; thus leading to increased extraction efficiency as illustrated in Figure 25.

4.2.3 *Effect of Stripping Agent and Concentration*

The choice of stripping agent is essential in the quantitative recovery of analyte. An inappropriate choice of stripping agent could result in incomplete recovery or alteration of chromium species during stripping. Therefore, the stripping efficiency was investigated for HNO_3 and NaOH for Cr(III) /(VI) species, respectively. The concentration of stripping agent is also important in an attempt to obtain complete recovery and maintain the original speciation state of the sample. Therefore, the concentration of the strip solution (HNO_3/NaOH) was varied to observe the optimal strip concentration necessary for extraction of chromium species. The optimum stripping agent concentration was determined and used in further investigations.

Figure 26 shows the effect of concentration of stripping agent (HNO_3) on the extraction efficiency of analytes. Cr(III) stripping is accomplished by substituting Cr(III) in the Cr(III) -DEHPA complex with protons and substitution of Cr(VI) with NO_3^- in the Cr(VI) -Aliquat ion pair [15]. Additionally, such a strong stripping agent at high concentrations of HNO_3 may lead to decomposition of DEHPA, thereby lowering stripping efficiency [56]. Incomplete stripping of Cr(III) may also be attributed to extraction of some hydrolysed/polymeric species, which could not be easily destabilized and extracted by DEHPA [56].

Nitric acid yielded unsatisfactory results (~80%) in the stripping of Cr(VI) from the Cr(VI) -Aliquat ion pair. Cr(VI) is also reduced to Cr(III) in acidic conditions and the

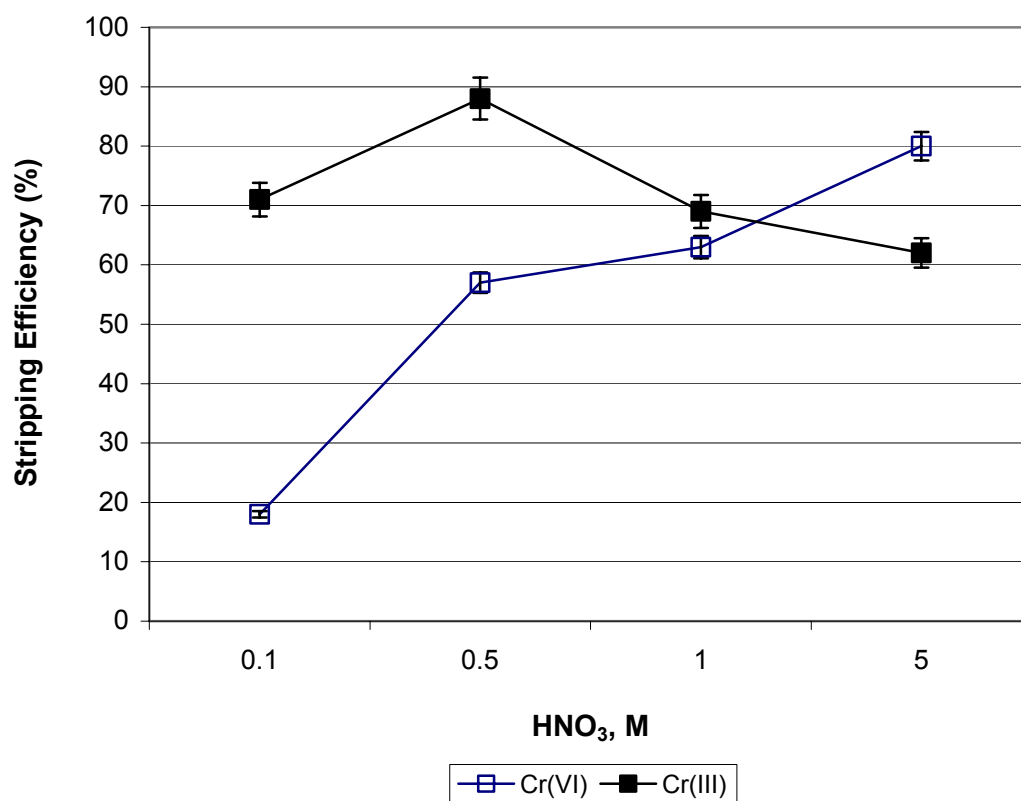


Figure 26.

Effect of HNO₃ Concentration on Cr(III)/(VI) Stripping (Liquid-liquid extraction):
1 v/v% Aliquat-336; 30 v/v% DEHPA; HNO₃ concentration varied from 0.5 M- 5 M.

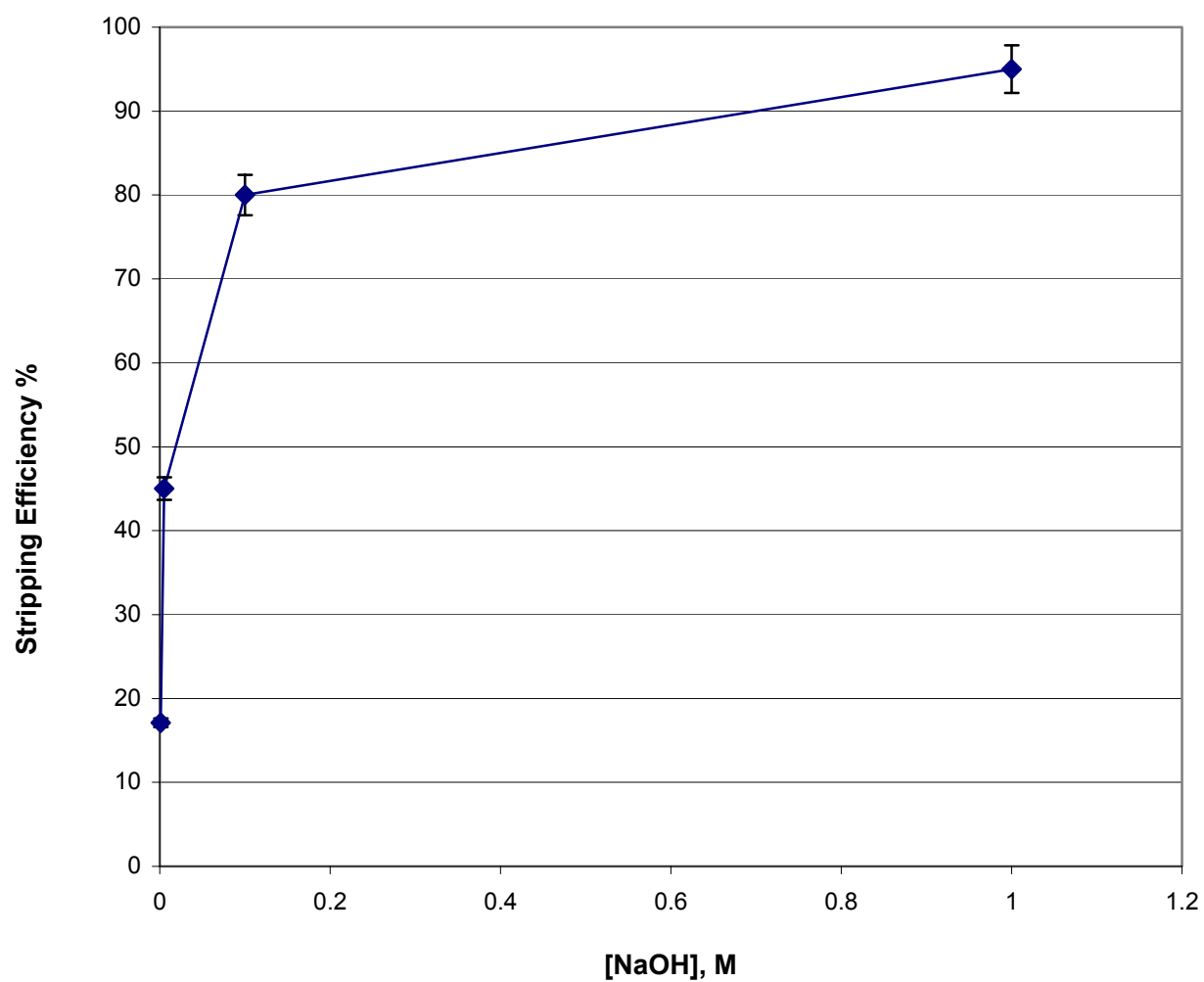


Figure 27.

Effect of NaOH Concentration on Cr(VI) Stripping (Liquid-liquid extraction):

1v/v% Aliquat; NaOH concentration varied from 0.001 - 1M

rate of reduction increases with decreasing pH [15]. Therefore, incomplete extraction of Cr(VI) species would be expected since Cr(VI) is being converted to Cr(III), which is not extractable with Aliquat-336. NaOH was investigated as an alternative strippant and yielded satisfactory results (~95%) as illustrated in Figure 27. Once Cr(VI) is in an alkaline solution, such as NaOH, it appears to be very stable [57]. In strong alkaline solutions, HCrO_4^- is converted to CrO_4^{2-} and CrO_4^{2-} becomes the major species of chromium [58]. If NaOH is used to increase pH, the concentration of HCrO_4^- is reduced and a more complete stripping process is achieved. The OH^- anion combines with Aliquat according to the following equation:



where AQ is *Aliquat-336*.

4.3 Surface Analysis

4.3.1 Physical Structure of Extractant Impregnated Membranes

The morphology of membranes governs their final properties which is why the nature of the surface and subsurface were important to this study. The most reliable and convenient tool for the study of the physical structure of the extractant impregnated membranes is the Scanning Electron Microscope. Scanning Electron Microscopy was used to study the surface and porous substructure of the membranes (both initially and impregnated). In this study two types of polymeric membranes were studied (Whatman[®]PP- polypropylene, Versapor[®]450, acrylic non woven copolymer). The polymeric supports of the Whatman[®]PP and Versapor[®]450 had a pore size of 0.20 and 0.45 μm respectively. Both membranes have a very rigid and stable structure and show zero or minimal expansion aqueous/inorganic solvents. The internal structures of the Versapor[®]450 and Whatman[®]PP membranes are shown in Figures 28 & 29. The general appearance of the Versapor[®]450 membrane pore structure is cylindrical while those of the Whatman[®]PP membrane appear to have a more “spongelike” structure.

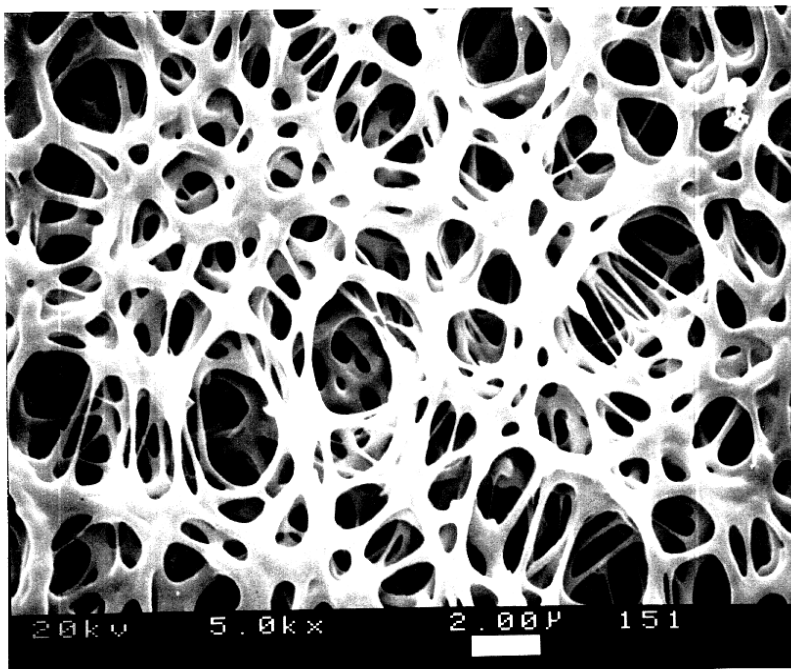


Figure 28. SEM Image of Internal structure of Versapor[®] 450 membrane; magnification x10000.

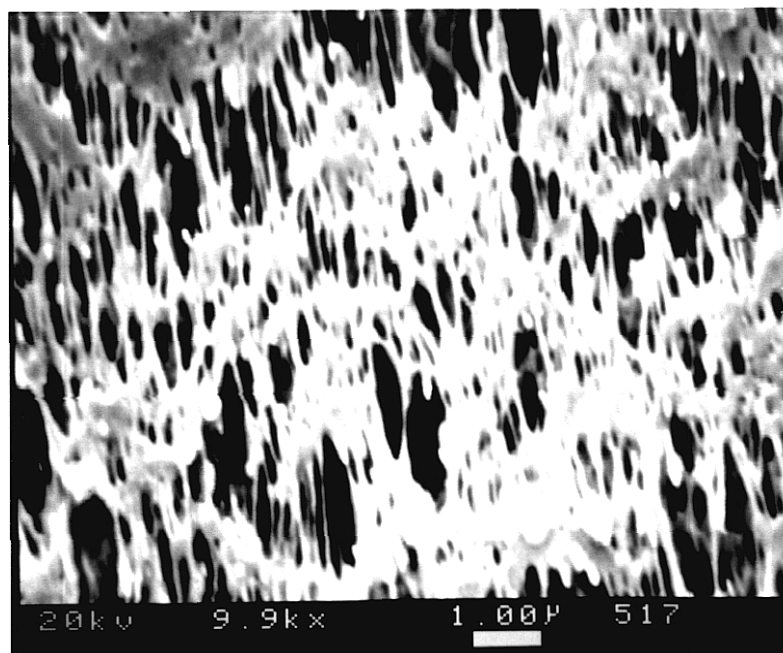


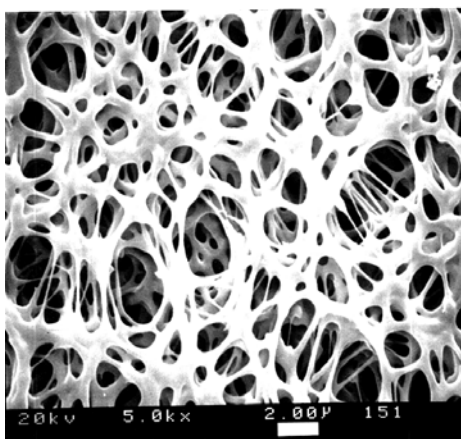
Figure 29. SEM Image of Internal structure of Whatman®PP membrane;
magnification x 10000

The surface and subsurface structure of the impregnated polymeric supports was next area of investigation. In the following figures, impregnation of the membranes revealed changes in the surface of the polymeric membranes. With increasing extractant concentration (0.5 & 1 v/v% Aliquat-336, 10 & 30 v/v% DEHPA) clusters of extractant appear on membrane pores and surface. The Aliquat extractant on the Versapor[®]450 membrane (Figure 30) coats the pore fibers of the membrane and continues to then fill up the pore diameters with a “spiderweb-like” appearance. The Aliquat extractant on the Whatman[®]PP membrane (Figure 31) appears to accumulate on the resin as clusters.

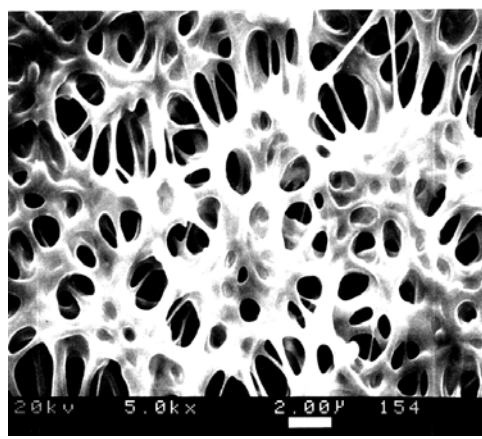
The DEHPA extractant on the Versapor[®]450 membrane (Figure 32) appears to cover the majority of the pore structure of the membrane with nodules starting to form at interstices with increasing extractant concentration. The DEHPA extractant on the Whatman[®]PP membrane (Figure 33) seems to take on a more glossy appearance that increases in coverage of the membrane surface with increasing extractant concentration. To the naked eye, the Aliquat-336 impregnated membranes have an opaque and powdery appearance. The DEHPA impregnated membranes appear to have a more transparent, glossy coating.

4.3.2 Elemental Composition of Extractant Impregnated Membrane Surface

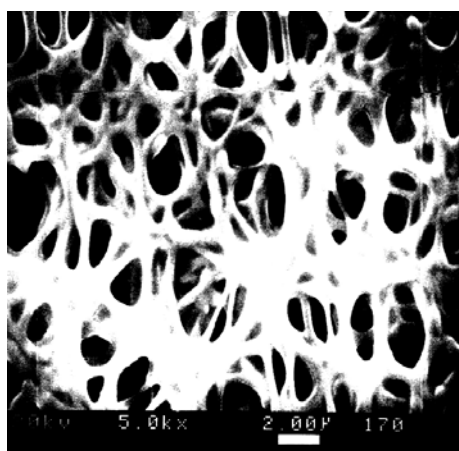
X-ray photoelectron spectroscopy was used to determine the presence of extractant on/in the membrane through changes in the elemental composition of the surface. XPS results of the plain Versapor[®]450 membrane (Table 10) indicate the major elements corresponding to the composition of the Versapor[®]450 membrane (71.5% C, 7.0% O, 12.0% N, and 9.5% Cl). Upon impregnation of



(a)



(b)



(c)

Figure 30.

SEM Images of Surface Changes on Versapor[®]450 membrane with Increasing Aliquat-336 Concentration: (a) plain Versapor[®]450 (b) 0.5 v/v% Aliquat-336 (c) 1 v/v% Aliquat-336; magnified x5000.

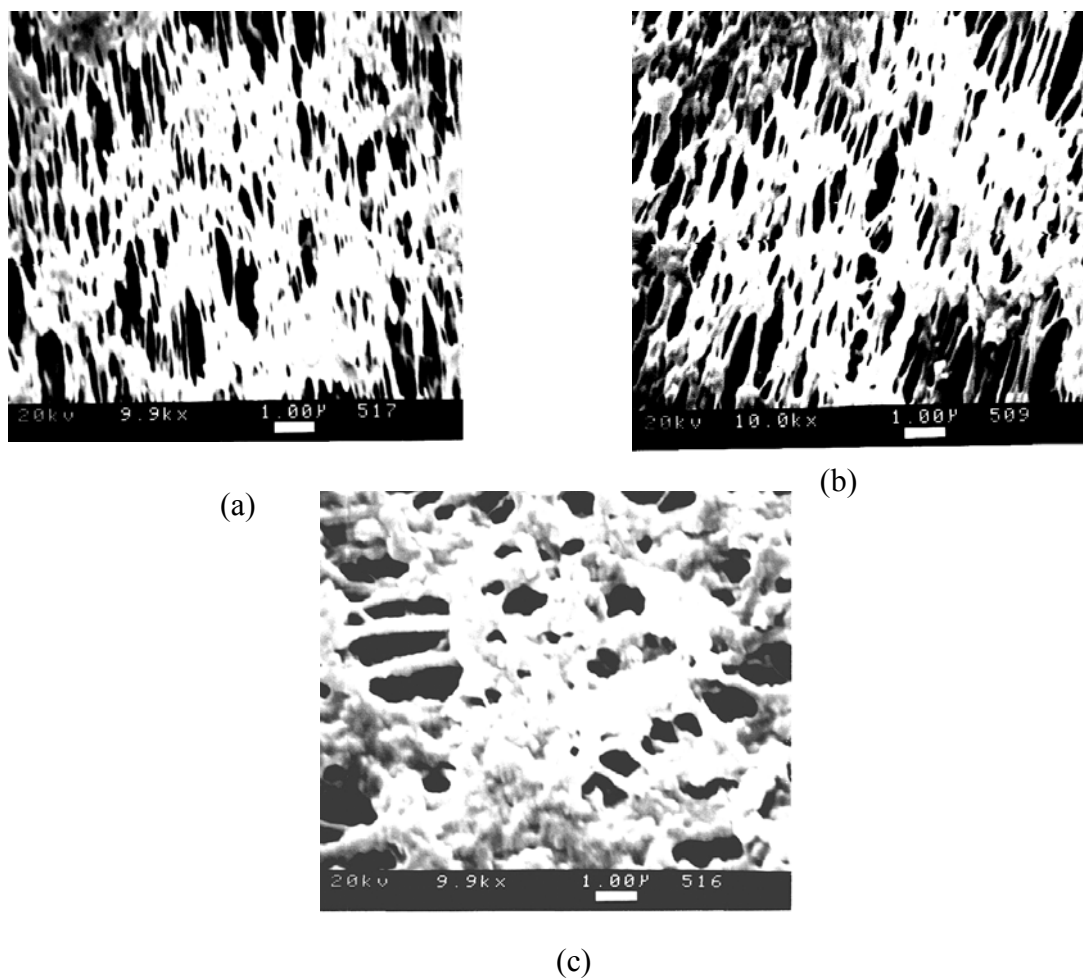
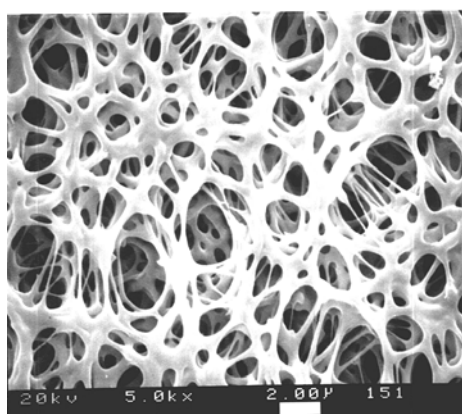
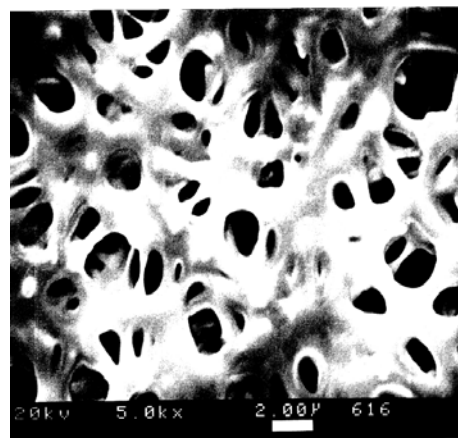


Figure 31.

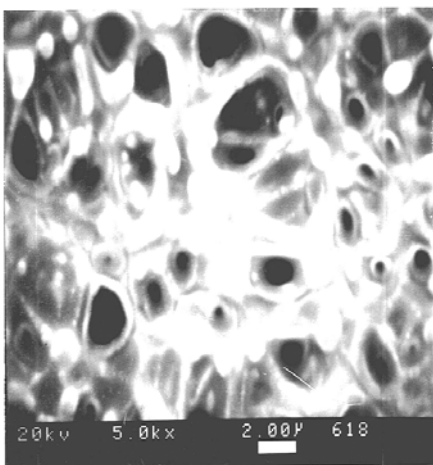
SEM Images of Surface Changes on Whatman® PP membrane with Increasing Aliquat-336 Concentration: (a) plain Whatman® PP (b) 0.5 v/v% Aliquat-336 (c) 1 v/v% Aliquat-336; magnified x5000.



(a)



(b)



(c)

Figure 32.

SEM Images of Surface Changes on Versapor[®]450 membrane with Increasing DEHPA Concentration: (a) plain Versapor[®]450 (b) 10 v/v% DEHPA (c) 30 v/v% DEHPA; magnified x5000.

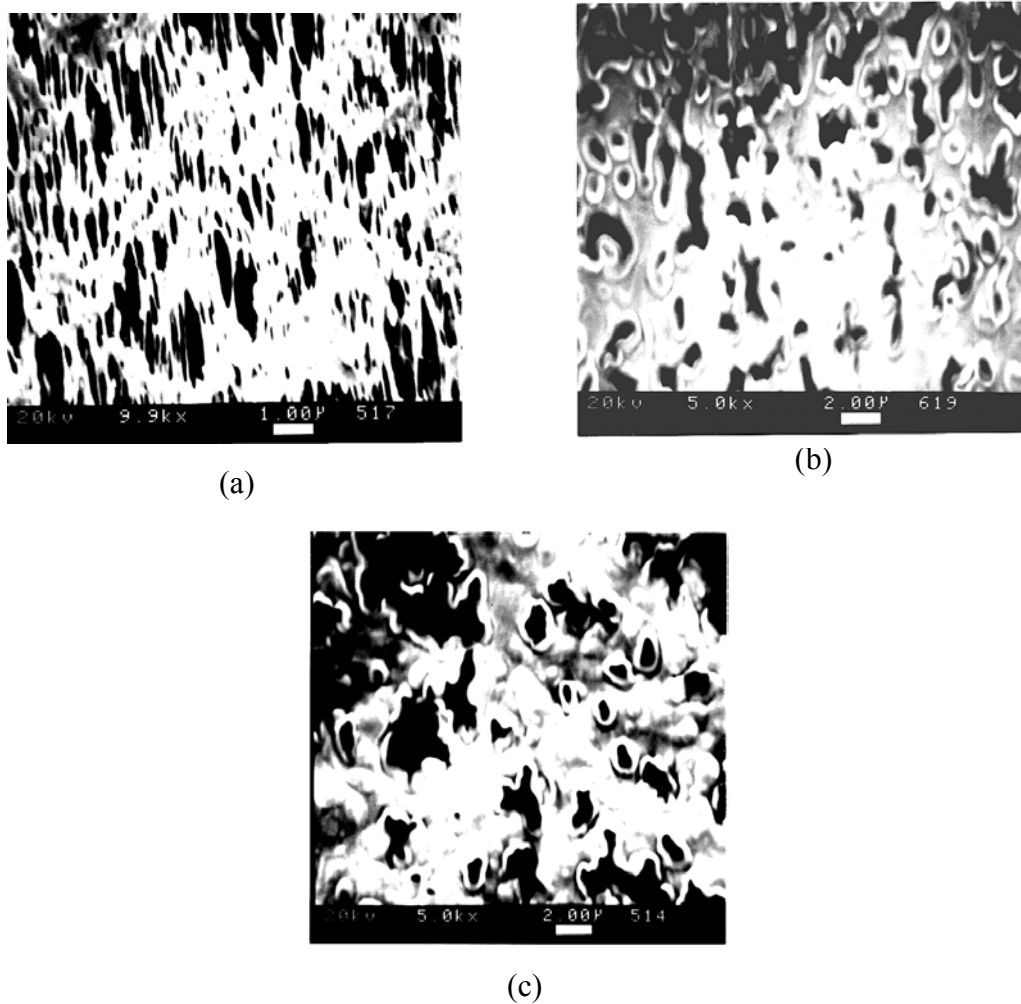


Figure 33.

SEM Images of Surface Changes on Whatman[®] PP membrane with Increasing DEHPA concentration: (a) plain Whatman[®] PP (b) 10 v/v% DEHPA (c) 30 v/v% DEHPA; magnification x5000.

1 v/v% Aliquat-336, there is an increase in the elemental percent of C (from 71.5-92.3 %) due to the additional carbon contributed from the number of carbons in the Aliquat-336 structure. The impregnation of Aliquat on the Versapor[®]450 membrane also decreases the elemental percent of Cl, O, and N (0.8% O, 3.6% N, and 3.3% Cl (Table 10). The acrylic framework of Versapor[®]450 contains C, O, N, and Cl and upon impregnation of Aliquat in/on the surface these elemental percentages decrease due to this physical adsorption, which covers the skeletal framework. Confirmation of the percent of coverage on the Versapor[®]450 membrane was determined through calculation of the atomic percentages contributed by each atom in the Aliquat molecule (last column on Table 10). The atomic percent contributions to the overall molecule were found to be 92.6% C, 3.7% N and 3.7% Cl. From this data, it can be concluded that nearly complete coverage was accomplished since the atomic percent of Aliquat accounts for majority of the C, N, and Cl reported on the surface of the membrane after impregnation.

XPS results of the plain Whatman[®] PP was 100%C, which would be expected from a polypropylene (hydrocarbon backbone) membrane (Table 11). After impregnation of 1 v/v% Aliquat-336 on the Whatman[®] PP membrane, the elemental composition changed to 94.3% C, 3.3% N, and 2.4% Cl (Table 11). Clearly, the presence of N and Cl on the surface is attributed to Aliquat-336, which is comprised of $\text{CH}_3(\text{CH}_2)_7\text{N}^+\text{Cl}^-$. The decrease in elemental percent of C is due to coverage of the polypropylene backbone of the support by the extractant. Again, the atomic percentages of C, N, and Cl in the Aliquat molecule (92.6% C, 3.7% N and 3.7% Cl) were compared to the atomic percentages obtained by XPS (94.3% C, 3.3% N, and 2.4% Cl), and the results show that virtually complete coverage was obtained in the impregnation of Aliquat on WPP.

Impregnation of 30 v/v% DEHPA on the Versapor[®]450 membrane indicated an elemental composition of 78.84% C, 3.36% P, and 17.80% O (Table 12). Presence of P and O is attributed to the DEHPA extractant, $(\text{C}_8\text{H}_{17}\text{O})_2\text{P}(\text{O})\text{OH}$. The elemental

percentages of the plain Versapor[®]450 membrane were 71.5% C, 7.0% O, 12.0% N, and 9.5% Cl. The elemental percent of C, N, Cl, and O from the Versapor support decreases due to coverage of polymeric framework. The elemental % of C increases, however, due to the increased carbon content contributed by the DEHPA molecule. The atomic percentages of P, O, and C attributed to the DEHPA molecule were calculated and found to be 76.2 % C, 19.0%O, and 4.8 P. Comparing these results to the atomic percentages reported from XPS (78.8%C, 17.8%O, and 4.8%P), shows virtually complete coverage was obtained in the impregnation of DEHPA on Versapor.

Impregnation of 30 v/v% DEHPA on the Whatman[®]PP membrane indicated an elemental composition of 76.32% C, 19.31% O, 4.37% P (Table 13). Presence of P and O is again attributed to the DEHPA extractant and studying the elemental percentages of the plain Whatman[®]PP membrane (100% C) we see that the elemental percent of C decreases due to DEHPA coverage and the presence of O and P occurs due to the structure of DEHPA. The atomic percentages of P, O, and C attributed to the DEHPA molecule were calculated and found to be 76.2 % C, 19.0%O, and 4.8 P. Comparing these results to the atomic percentages reported from XPS (76.3.8%C, 19.3.8%O, and 4.4%P), shows that nearly complete coverage was obtained in the impregnation of DEHPA on WPP.

4.4 *Effect of pH on Cr(VI)/(III) Extraction Efficiency*

Chromium speciation is highly variable upon pH. This change in speciation attributed to pH may have a drastic effect on the extraction efficiency of the system. The optimal pH conditions of the extraction technique may not reflect the natural pH of chromium species found in environmental matrices. Therefore, the influence of pH on extraction efficiency was investigated. Extraction results of the effect of pH are shown in

Table 10. XPS Elemental Concentration of 1 v/v% Aliquat Impregnated on Versapor[®] 450 Membrane.

	Concentration (%)		
Element	Initial	After Impregnation	Calculated Aliquat Atomic %
C	71.5	92.3	92.6
O	7.0	0.8	—
N	12.0	3.6	3.7
Cl	9.5	3.3	3.7

Table 11. XPS Elemental Concentration of 1 v/v% Aliquat Impregnated on Whatman® PP Membrane

	Concentration (%)		
Element	Initial	After Impregnation	Calculated Aliquat Atomic %
C	100	94.3	92.6
N	nd	3.3	3.7
Cl	nd	2.4	3.7

Table 12. XPS Elemental Concentration of 30 v/v% DEHPA Impregnated on Versapor[®]450 Membrane

	Concentration (%)		
Element	Initial	After Impregnation	Calculated DEHPA Atomic %
C	71.5	78.8	76.2
O	7.0	17.8	19.0
N	12.0	nd	—
Cl	9.5	nd	—
P	nd	3.4	4.8

Table 13. XPS Elemental Concentration of 30 v/v% DEHPA Impregnated on Whatman[®] PP Membrane

	Concentration (%)		
Element	Initial	After Impregnation	Calculated DEHPA Atomic %
C	100	76.3	76.2
P	nd	4.4	4.8
O	nd	19.3	19.0

Figure 34. In Cr(VI) extraction at pH values ~ 2 , extraction efficiency decreases possibly due to an increase in protons concentration in the feed solution that forms species like $\text{H}_2\text{Cr}_2\text{O}_7$ or HCr_2O_7 . These species may not ionize completely at high acid concentration to form a complex with the Aliquat cation resulting in a decrease in extraction efficiency [36]. Thus, extraction of Cr(VI) ions will decrease. HSO_4^- , from H_2SO_4 used to adjust pH, is also likely to compete with HCrO_4^- for ion pairing with cationic Aliquat-336 [24]. Additionally, Cr(VI) is reduced to Cr(III) in acidic conditions and the rate of reduction increases with decreasing pH [15]. At high pH values larger than 6, extraction efficiency drops more likely due to the decrease in fractions of HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$ with increasing pH.

In Cr(III) extraction at pH values ~ 2 , we observe a decrease in extraction efficiency more than likely due to proton competition with cationic Cr(III) for DEHPA [23] (Figure 35). Additionally, at low pH values less DEHPA ion exchanger is available, DEHPA has been protonated [31]. The increasing concentration of H^+ at low pHs present a competition between H^+ and Cr(III) for available binding sites on DEHPA. Therefore, extraction efficiency would be expected to decrease. At high pH values >6 , metal hydroxide complexes with low solubility may be formed in the source interfering with Cr(III) extraction [15]. The pH of the source is critical for Cr(III) owing to hydrolysis reactions. Below pH 6.5, the dominant species is CrOH^{2+} while insoluble $\text{Cr}(\text{OH})_3$ species dominate between pH of 6.5 to 10.5 [15]. Furthermore, the solubility of DEHPA in the source increases with pH due to its dissociation [47].

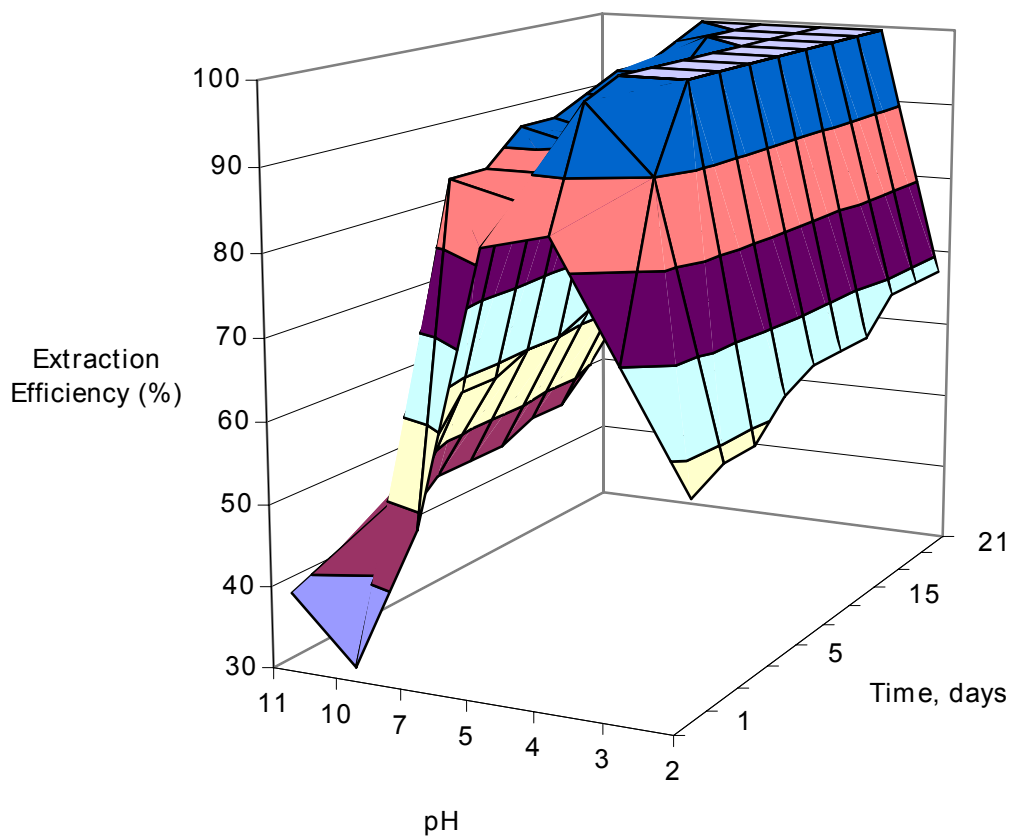


Figure 34.

Effect of pH on Cr(VI) Extraction: 1v/v% Aliquat-336; source pH varied from 2-11; source concentration 50 ppm Cr(VI). Effective pH range for Cr(VI) extraction is from 3-6.

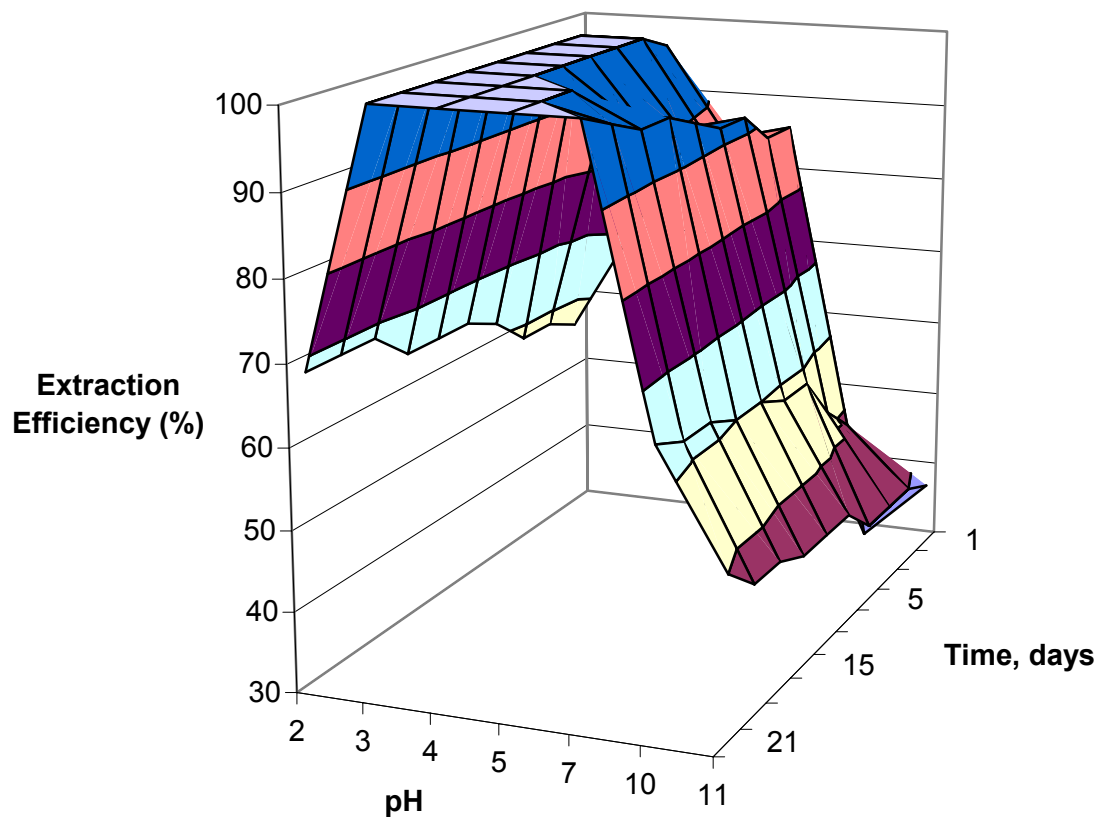


Figure 35.

Effect of pH on Cr(III) Extraction Efficiency: 30 v/v% DEHPA; source pH varied from 2-11; source concentration 50 ppm Cr(III). Effective pH range for Cr(III) extraction is 3-5.

4.5 *Effect of Competitive Anions on Cr(VI) Extraction Efficiency*

Extractants often used in solvent and membrane extraction techniques rarely exhibit complete selectivity for one solute over all others in solution. In the presence of competitive anions, chromium (VI) may show variable extraction efficiency. It is important to study the effect of competitive anions on Cr(VI) extraction due to their ubiquitous presence in environmental matrices. In this set of experiments, the extraction of Cr (VI) was investigated in the presence of three common interfering anions (NO_3^- , SO_4^{2-} , Cl^-). The extraction results are presented in Figure 36. There are significant differences in the extraction efficiencies of the three sodium salts. The NO_3^- anion posed the greatest interference to Cr(VI) extraction, reducing extraction efficiency to 75%. The Cl^- and SO_4^{2-} anion showed little/no interference of Cr(VI) extraction, with complete recovery of Cr(VI) after 7 days. The relative affinities of these three anions to Aliquat-336 are in the order of $\text{NO}_3^- > \text{Cl}^- > \text{SO}_4^{2-}$, which corresponds to the complexing ability given by Ritcey and Ashbrook [59].

4.6 *Effect of NO_3^- Concentration on Cr(VI) Extraction Efficiency*

Due to the NO_3^- anions great affinity to Aliquat-336, its effect on extraction was investigated to further understand the influence of NO_3^- on Cr(VI) extraction. Cr(VI) solutions with different NaNO_3 concentrations (ionic strength 0.001 M -1 M) were prepared. The results indicated in Figure 37 show that with an increase in NO_3^- concentration extraction efficiency decreases. The increase in ionic strength of the aqueous feed introduces more competition between the NO_3^- anion and Cr(VI) oxyanions for Aliquat-336. Aliquat-336 has high affinity for NO_3^- , thus Cr(VI) extraction would be expected to decrease in the presence of increasing amounts of NO_3^- .

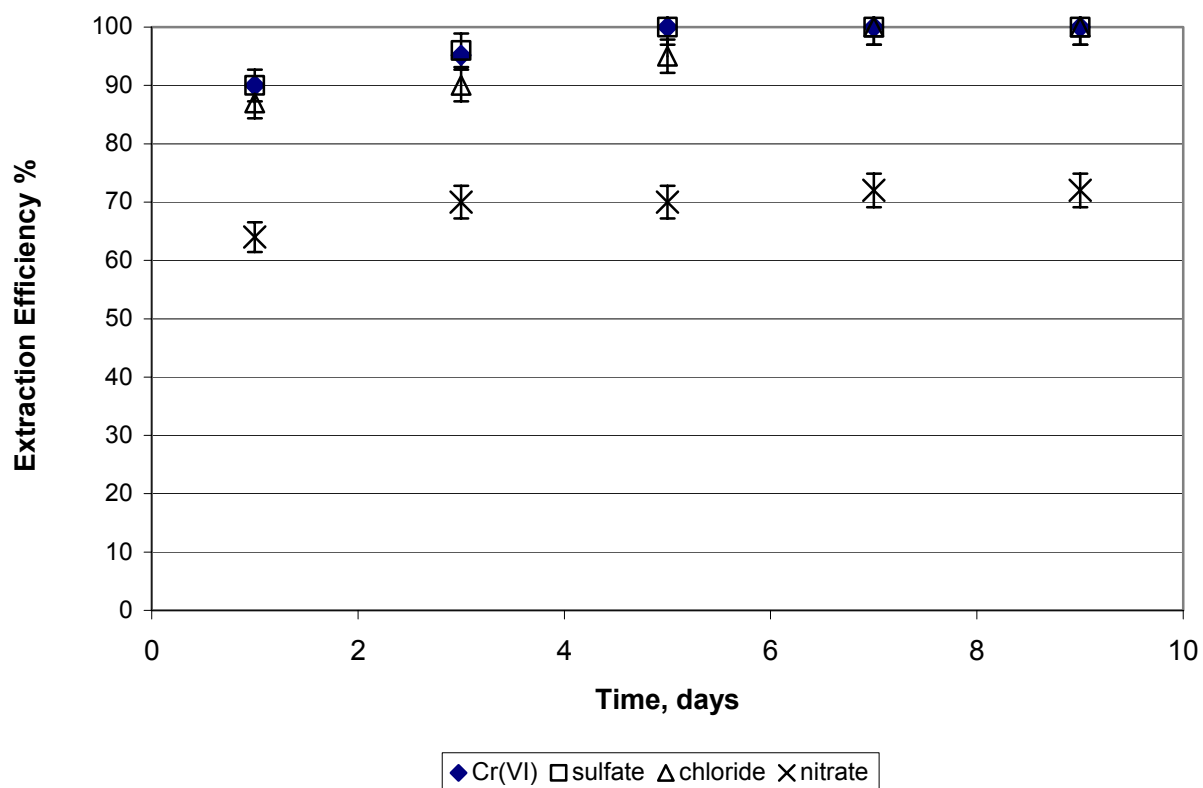


Figure 36.

Effect of Competitive Anions: 1v/v% Aliquat-336; source composition 50 ppm Cr(VI) in 0.1 M NaCl, NaNO₃, Na₂SO₄. Aliquat affinity for competitive ions over Cr(VI) follows the order NO₃⁻ > Cl⁻ > SO₄²⁻.

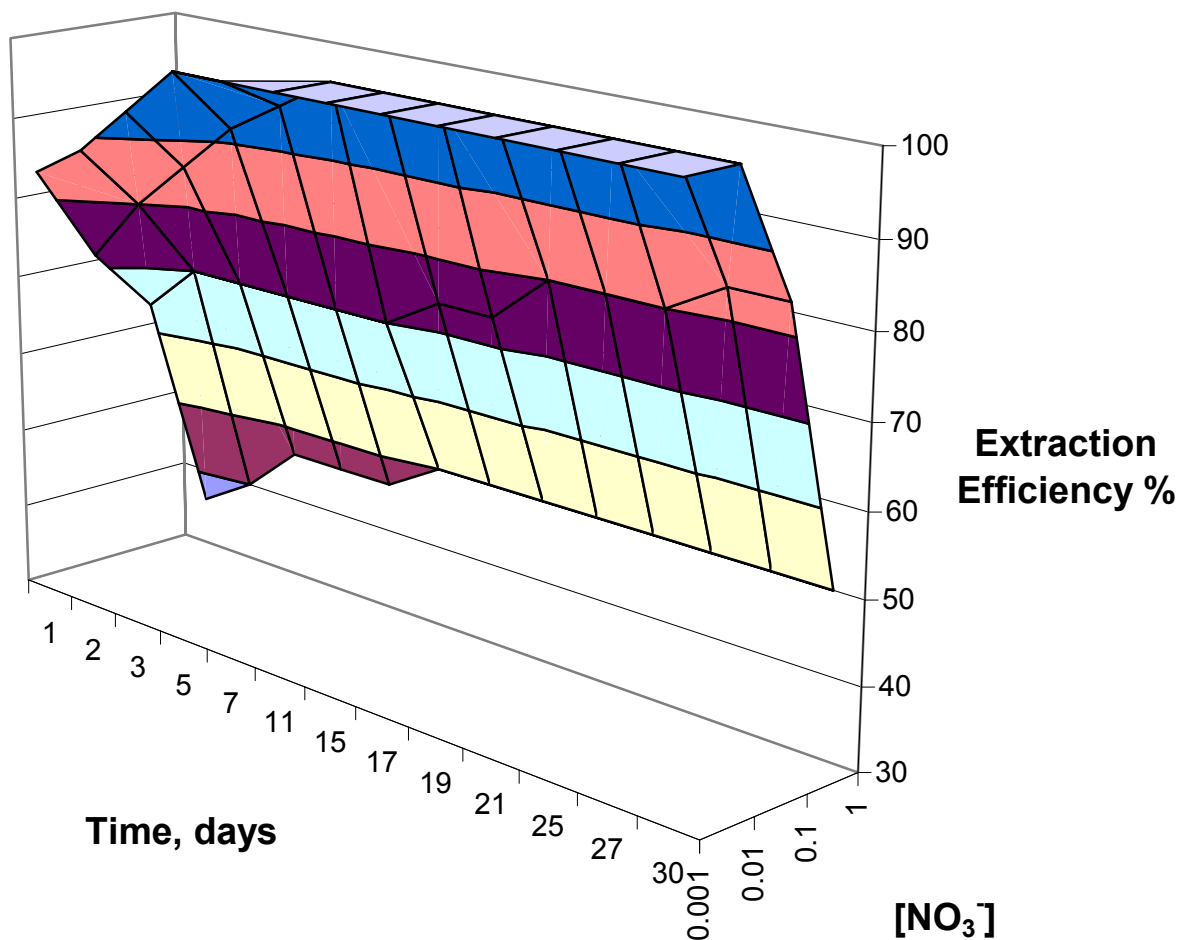


Figure 37.

Effect of NO_3^- on Cr(VI) Extraction Efficiency: 1v/v% Aliquat-336; source composition 50 ppm Cr(VI); NaNO_3 concentration (0.001-1M NaNO_3). Increase in NO_3^- concentration decreases extraction efficiency.

4.7 *Effect of Competitive Cations on Cr(III) Extraction Efficiency*

Chromium (III) is commonly found in close association with other cationic constituents in environmental matrices. Many of which exhibit similar chemistry to Cr(III). As a result, Cr(III) extraction efficiency may be highly dependent upon the presence of other cationic constituents in solution. Therefore, the extraction of Cr (III) was investigated in the presence of the interfering cations (Fe^{3+} , Ni^{2+} , Al^{3+} , Mg^{2+}). The cations Fe^{3+} and Al^{3+} were investigated due to their similar atomic radii (atomic radii of Cr-64, Al-67, Fe- 54pm) [22]. Cr(III) will be also found in close association with Al and Fe due to their prevalence in the earth's crust. In surface environments, hydrous oxides of Al and Fe are present in significant amounts. However, in subsurface environments, the presence of these hydrous oxides is negligible to anoxic conditions. As shown in Figure 38, in the presence of Fe and Al, the extraction efficiency is reduced to 45%. Fe^{3+} posed the greatest interference to Cr(III) extraction, with only 45% extraction of Cr(III) occurring within the 30 days.

The ionic potentials of the trivalent ions are close enough together that substitution of one for another occurs in many mineral and organic structures [22]. The affinity of Al(III) / extraction over Cr(III) is possibly due to the kinetics of extraction between the two cations with DEHPA. Although the extraction of Cr(III) by DEHPA in the absence of other competitive cations is rapid, Al(III) has been reported to form even faster complexes with DEHPA, possibly due to the greater ionic potential of aluminum. Chromium (III) forms a multitude of complexes, both organic and inorganic. However, it is slower in forming them compared with aluminum. Once the complex between DEHPA and Cr(II) has formed however, the result is stronger bonding, and hence chromium has replaced its aluminum analog for the tanning of leather. The presence of the cations at a 50 mg/L concentration of Fe^{3+} , Ni^{2+} , Al^{3+} , Mg^{2+} was shown to reduce Cr(III) extraction efficiency to ~60% as presented in Figure 38. DEHPA is also well-known extractant for divalent cations [24].

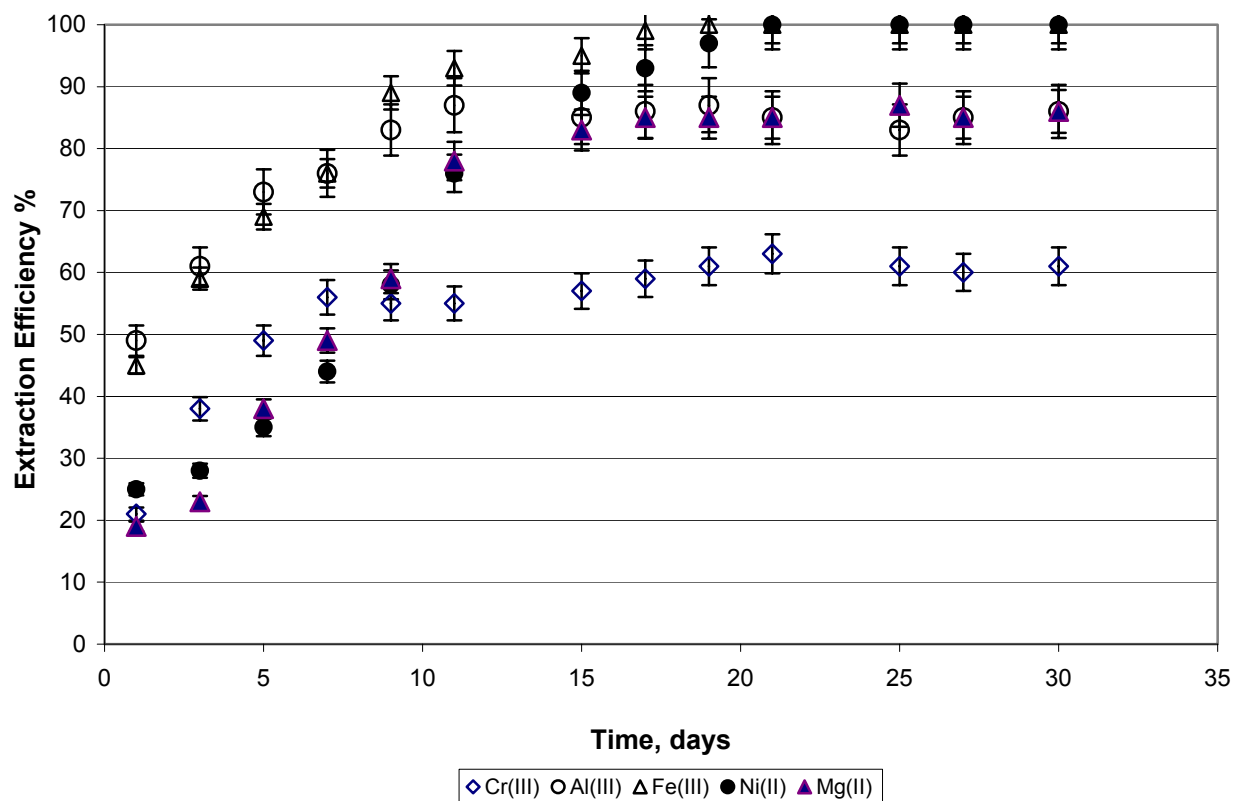


Figure 38. Effect of Competitive Cations on Cr(III) Extraction: 30v/v% DEHPA impregnated membrane; source composition 50 ppm Cr(III), Al(III), Fe(III), Ni(II), Mg(II); pH of source 2.9

4.8 *Effect of Source Concentration*

Extraction efficiency may be dependent upon the concentration of analyte in the source phase. Extraction efficiency may vary at high/low concentrations of analyte, which in turn may limit the application of the technique. Therefore, the influence of the source concentration (*i.e.* the solution containing the metal ion) on extraction efficiency was studied to observe the optimal source concentration necessary to achieve optimum extraction of chromium species. The concentration dependence of extraction efficiency was investigated by varying the source concentration from 1-50 mg/L of Cr(III)/(VI). The results are illustrated in Figure 39. The extraction efficiency of Cr(III) and Cr(VI) are shown to be independent of initial source concentration over the concentration range tested.

4.9 *Membrane Lifetime and Stability*

Membrane instability is dependent upon many factors including solubility of the extractant in the aqueous phase, flow of the source phase, adherence to the polymeric support, *etc.* Extraction efficiency of the system would be highly dependent upon the stability of the impregnated membrane under these varying conditions. Therefore, the stability of the extractant impregnated membranes was studied to assess the applicability and lifetime of the system. The stability of the prepared membranes were determined by the weight loss method, in which the amount of organic within the membrane pores is obtained by weighing the impregnated membrane before and after equilibration with the aqueous phase. The membrane was termed “degraded” after equilibration with the aqueous phase.

To observe the effect of membrane preparation on membrane stability, an experiment was conducted in which “wet” surface versus “dry” surface impregnation was compared. “Wet” surface membranes are prepared with wet outer surfaces. The organic phase consisting of diluent and extractant are not allowed to evaporate. Dry surface membranes are free of organic wetting. The organic phase is allowed to evaporate under

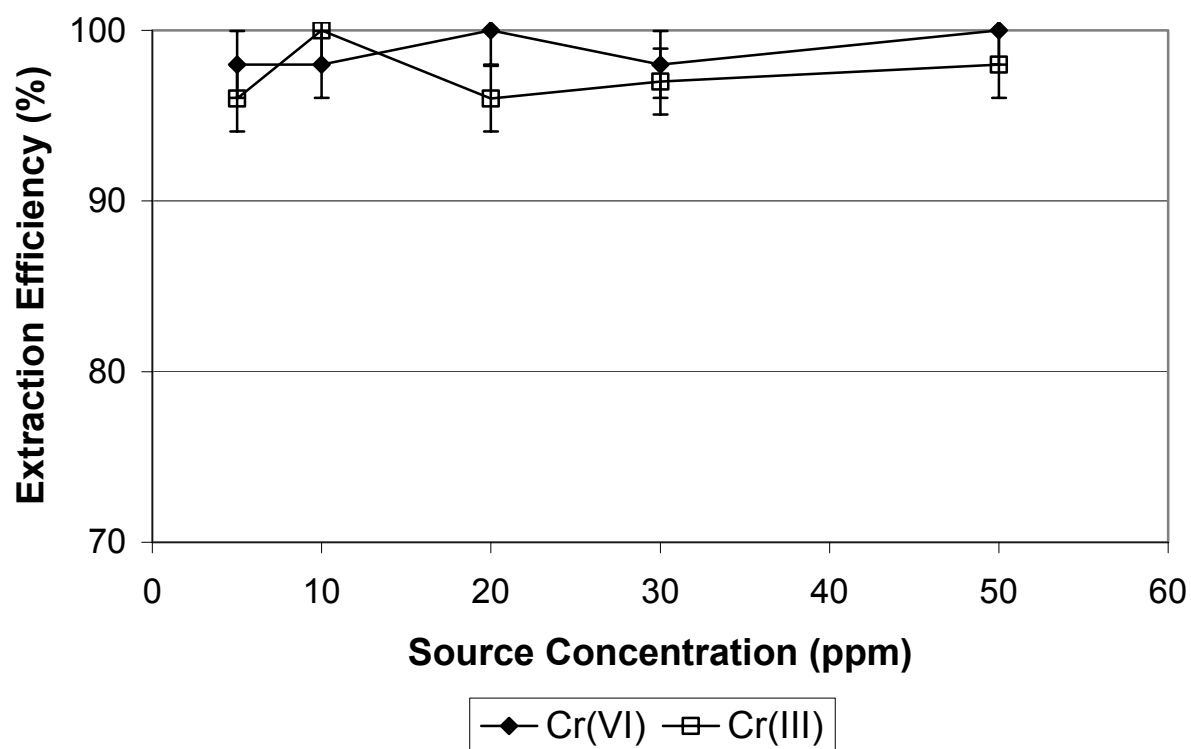


Figure 39. Effect of Source Concentration on Cr(III)/(VI) Extraction: 1v/v% Aliquat, 30v/v% DEHPA; pH=3.5.

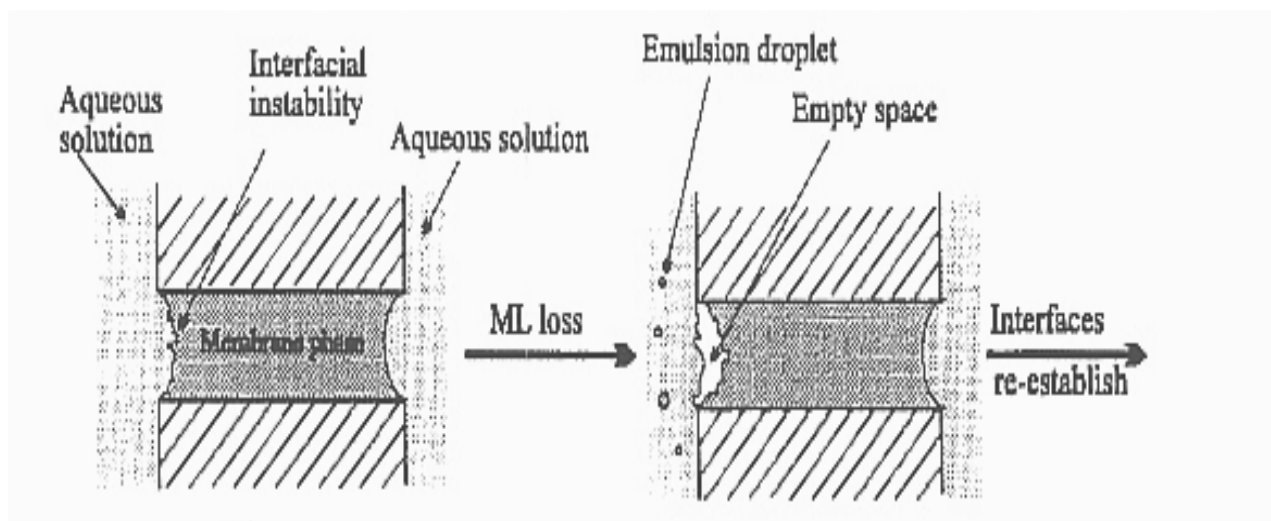


Figure 40. Membrane Extractant Loss [54].

	Dry (WPP)	Wet (WPP)	Dry (Versapor)	Wet (Versapor)
Membrane (g)	0.3429	0.5723	0.1423	0.2198
ML% at 24hrs	1.3% +/- 0.3	3.2% +/-0.5	2.9% +/- 0.6	14.9% +/-0.65
ML% at 24hrs (100rpm)	2.6% +/- 0.4	5.4% +/- 0.7	5.9% +/- 0.5	20.7% +/- 0.8

Table 14.

Membrane Extractant Loss: Wet Surface versus Dry Surface Membranes

Wet surface membranes suffer from higher percentage of extractant loss from membrane due to increased loss of extractant from membrane to aqueous phase.

ambient conditions. The two impregnation techniques were simply immersed into deionized water and visual observations were first taken to observe any extractant loss to the aqueous phase. In the case of the wet surface membrane, visual loss of the organic phase to the aqueous phase was clearly observed. The “wet” surface impregnated membrane, once immersed in the aqueous phase, produced emulsions in the aqueous phase. Membrane loss has been reported by Zha *et. al.* to be primarily attributed to emulsion formation, which results in loss of extractant from the support to the aqueous phase as shown in Figure 40 [54]. This visual loss of extractant from the membrane to the aqueous is a clear indication of membrane instability, which in turn would result in a decreased extraction efficiency for the system. Impregnated membranes prepared by the “wet” surface method would require routine regeneration of the membrane with fresh extractant to maintain extraction efficiency.

The dry surface membranes produced no such emulsion formation visible to the naked eye. Membrane loss by simple immersion was also calculated using the weighing method described previously. The results are reported in Table 14. Membrane loss with time was also studied and the results are also illustrated in Table 14. Membrane loss was also studied as a function of the stirring speed of the aqueous solutions. The loss of extractant to the aqueous phase at equilibrium was compared to extractant loss observed at 100 rpm. It was found that increased stirring speed increased the loss of extractant to the aqueous phase. Takeuchi *et. al.* revealed that the lifetime of impregnated membranes become shorter with an increase of the linear velocity of the aqueous solution [60]. Neplenbroek *et. al.* determined that increasing the stirring speed increases the tangential velocity across the interfaces of the aqueous solutions and the membrane [61]. Also, increasing the stirring speed enhances the turbulence in the aqueous solutions and thus increases the shear force at the interfaces between the membrane and the aqueous solutions [61]. This in turn would increase the loss of extractant from the membrane to the aqueous phase and therefore decrease extraction efficiency.

Increased stability of the Whatman[®] PP membrane was attributed to the pore size of the support. Stability of membrane supports with smaller pore size has been found to produce longer lifetimes [54]. The hydrophobicity of the Whatman[®] PP membrane has also been found to contribute to the increased stability of impregnated membranes. Hydrophobic supports have been discovered to be a more stable support for the organic membrane liquid, resulting in reduced extractant loss to the aqueous phase; thereby, increasing the stability and lifetime of the membrane system.

Chapter 5

5. Column Study

5.1 Introduction

The batch and membrane studies investigated thus far indicate the promising potential for extractant impregnated membranes to separate, trap, stabilize and preserve individual chromium species. The full applicability of the technique will be dependent on a number of factors, which include design, performance of the system under simulated environmental conditions, and stability of the membranes under such conditions. The design of the system is important in that it determines the full range of applications the technique may find use. Complicated design and difficult manipulation will limit the user capability to expert or experienced individuals. Tedious and cumbersome techniques, which employ several steps and extensive attention, will limit the technique from use in many industries and laboratories.

The stability and lifetime of the system when applied to complex conditions, such as environmental matrices, is important in that the lifetime of the technique may be shortened and as a result extraction efficiency is reduced. Earlier investigations regarding membrane stability and lifetime showed majority of the extractant loss to occur within the first 24 hrs. After which, the loss waned. The extractant loss observed had little effect on extraction efficiency as extraction efficiencies of 98-100% were achieved. Research studies by Neplenbroek *et. al.* and Takeuchi *et. al.* have shown that increasing the stirring speed or flow rate increases tangential velocity across the interfaces of the aqueous solutions and the membrane. The lifetime of impregnated membranes reportedly become shorter with an increase of the linear velocity of the aqueous solution. Membrane stability was indeed found to be dependent upon stirring speed across the interfaces of the membrane and aqueous solution as observed earlier this work. Groundwater, wastewaters, and other sites of contamination will undoubtedly be subject to some perturbation or flow, thus the stability of these extractant membranes under these simulated conditions is another area of investigation in this Chapter.

The performance of the system, in terms of extraction efficiency, must be sufficient for the potential application. Laboratory studies have indicated the excellent performance of these extractant impregnated membranes under batch and membrane studies, but the next area of concern is how these extractant impregnated membranes perform when utilized under more complex conditions such as contaminated environmental matrices. Extraction efficiency of chromium species has already been shown to be dependent upon cationic and anionic interferents, pH, ionic strength and a number of other factors encompassing the preparation of the membranes. As a result of these investigations, extraction efficiency is expected to vary but to what degree is the next area of study and is the purpose of this Chapter.

5.2 *Column Design*

The design of the column was investigated for the potential application of multilayer sampling (MLS) technology. The basis of the application is to use the extractant impregnated membranes as a sampling tool within the multiplayer sampling apparatus. An illustration of the multiplayer sampler is shown in Figure 41. The MLS consists of individual chambers located perpendicular along the axis of the column. Each chamber allows a representative sample of the external aqueous phase to be obtained at the layer sampled. As a result, stratification of the sampled site can be obtained which is very useful when determining the source of contamination. The contaminated site subsurface is sampled by drilling a hole and inserting the MLS down within the hole (Figure 42). The selective ion traps will be incorporated within each chamber and selectively trap Cr(VI) and Cr(III) species.

The selective ion trap assembled in the laboratory was designed to mimic the operation of the multiplayer sampler to observe the extraction efficiency of the sampling membranes under simulated conditions much like those encountered when using the MLS. The extraction efficiency of the extractant impregnated membranes within the column assembled in the laboratory was explored to study the performance of these membranes for potential field application. The first area of concern focused on the design

Multilayer Sampler (MLS)

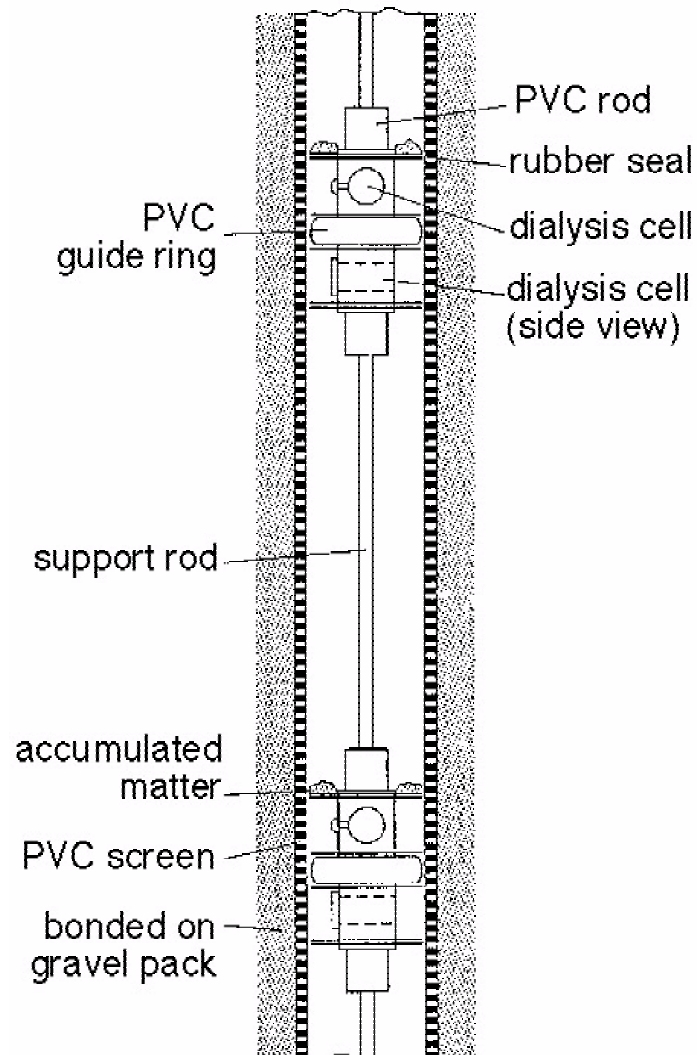


Figure 41.
Multilayer sampler (MLS)



Figure 42.
Field Application of Multilayer Sampler (MLS)

of the column and the incorporation of the impregnated membranes within this column. A cast plastic column was modified to accommodate the selective ion trap, which consisted of the Aliquat-336 and DEHPA extractant impregnated membranes. The inner diameter of the column was 2.5 cm and the length of the column was 8 cm. This yielded a total volume of 39.25 cm³. A 2" section was cut to accommodate the selective ion trap (Figure 43). The design of the column was based upon a diffusive sampler in which the basic unit of the column consists of the selective ion trap (2" mid-section). The entrance/exit nylon membranes at the top and bottom of the column filtered and prevented colloidal material from entering the column. When the selective ion trap was exposed to an external environment of water (*i.e.* the source solution), an extractive process of all target analytes from the external water into the impregnated membranes started. This process continued until equilibrium was reached (no further increase in extraction efficiency after 24 hr period). At this point, the extractant impregnated membranes contained a representative sample of the targeted analytes. The 1st ion trap in the cell was impregnated with the Aliquat-336 extractant, which is selective for the Cr (VI) anion, and was placed after the entrance membrane. The 2nd ion trap was impregnated with di-(2-ethylhexyl phosphoric acid (DEHPA), which is selective for the Cr (III) ion, and was placed after the Aliquat-336 impregnated membrane. Aqueous samples then exited through the outlet membrane at the end of the cell.

5.3 Column Membrane Stability

Membrane instability is reported to be dependent upon many factors including solubility of the extractant in the aqueous phase, flow of the source phase, adherence to the polymeric support, *etc.* Extraction efficiency of the system would be highly dependent upon the stability of the impregnated membrane under these varying conditions. Therefore, the stability of the extractant impregnated membranes when incorporated into the column flow cell assembly was studied in order to assess the

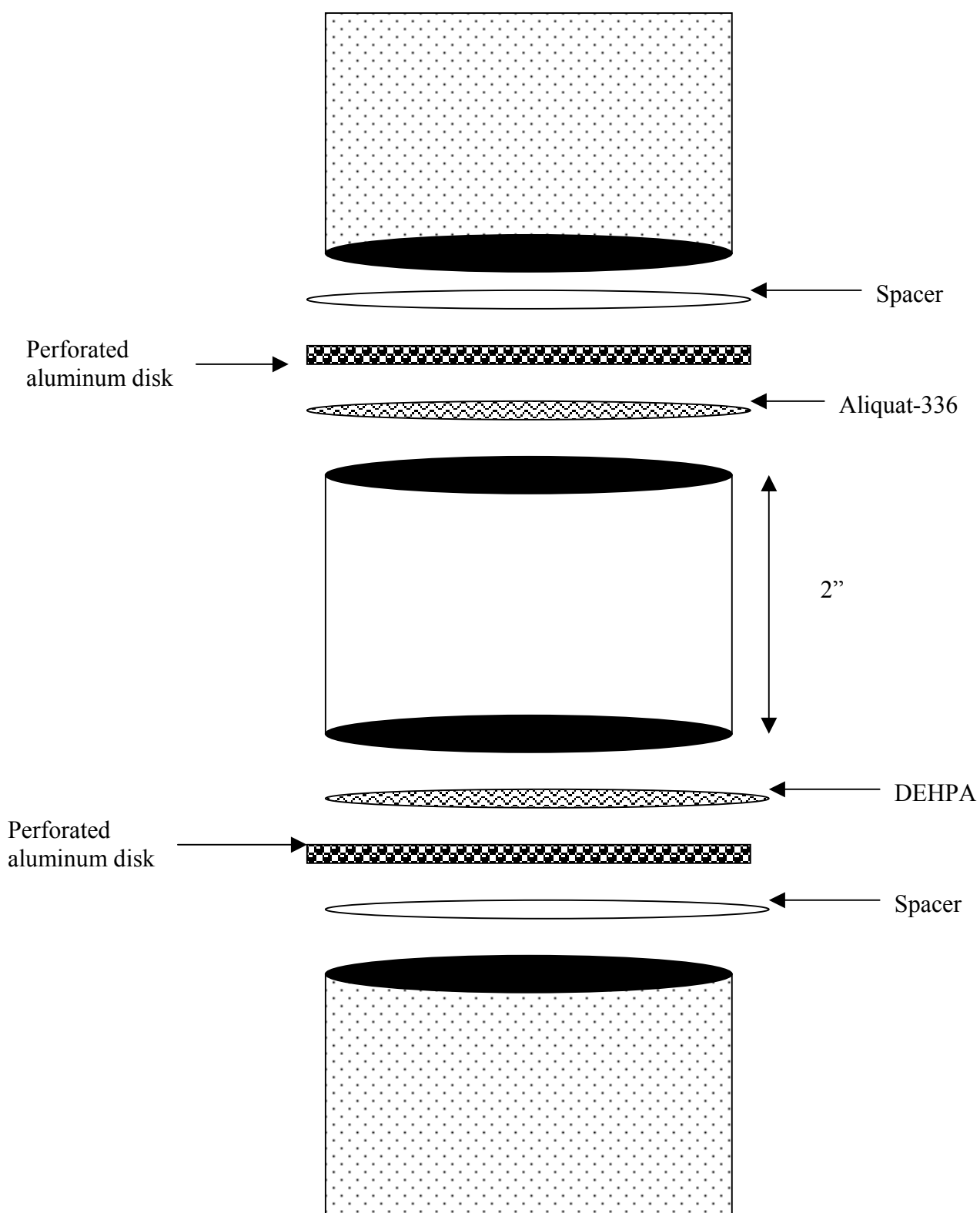


Figure 43. Selective Ion Trap.

applicability and lifetime of the system. Increased loss of extractant (*i.e.* dissolution of the extractant into the aqueous phase) will diminish the efficiency of the system owing to a lower concentration of the extractant in the membrane. The extractant loss within the membrane was determined by the weight loss method, in which the amount of extractant contained within the membrane pores is obtained by weighing the impregnated membrane before and after equilibration with the aqueous phase. A flow of 1 ml/min was continuously passed through the column flow assembly for 24 hrs. After which, the degraded membranes were taken from the setup and the percent of extractant loss was determined by the weighing method.

The percentage of extractant loss within the membrane using the column was compared to that of extractant loss by simple immersion and the results are shown in Table 15. The results show that flow rate through the membrane increases extractant loss within the membrane most likely due to the effect studied by Neplenbroek *et. al.* in which an increase in tangential velocity across the interfaces of the aqueous solutions and the membrane enhances extractant loss. This increased extractant loss observed was an area of concern in that drastic loss of extractant would in turn result in a dramatic decrease of extraction efficiency of the system. Therefore, the extraction efficiency of the flow cell assembly was the next area of investigation.

5.4 Column Cr(III)/(VI) Extraction using Standard Solutions

The extraction efficiency of the flow cell assembly for Cr(VI)/(III) species in standard solution is shown in Figure 45. As shown, we observe a maximum extraction efficiency of 95% and 88 % for Cr(VI) and Cr(III) respectively after 3 days. In comparison to the extraction efficiencies obtained in batch experiments, we see that removal of Cr species using the column results in a 8% and 16% decrease in extraction efficiency for Cr(VI) and Cr(III) respectively. This is predominantly attributed to the

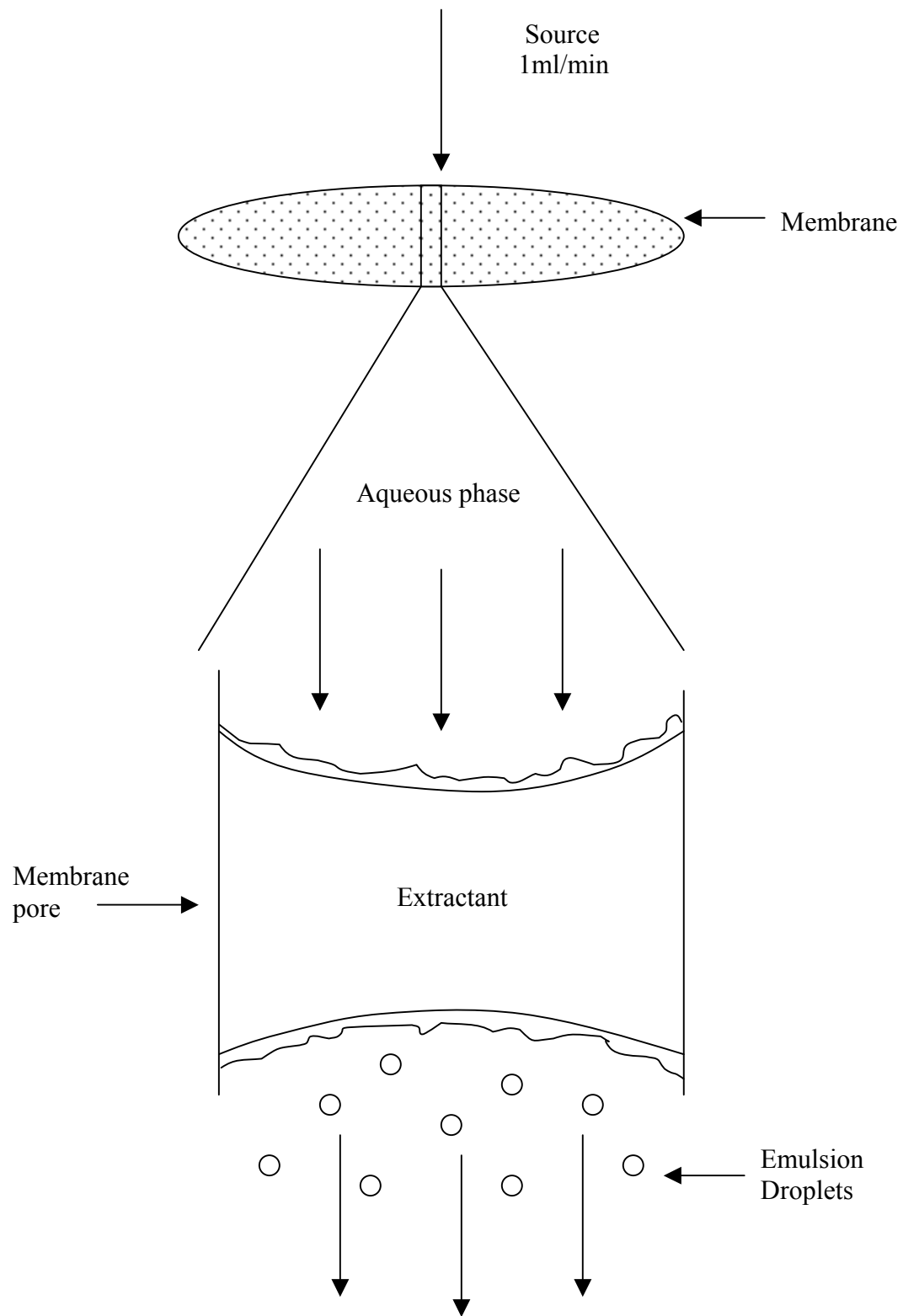


Figure 44. Extractant Loss from Membrane using Column.

	Whatman [®] PP
ML% at 24hrs (equilibrium)	2.9 % +/- 0.5
ML% at 24hrs (1ml/min)	5.3 % +/- 0.8

Table 15. Membrane Extractant Loss: WPP membrane (1 v/v% Aliquat, 30 v/v% DEHPA).

enhanced loss of extractant to the aqueous phase, which in turn results in a decrease in extraction efficiency. This increased loss of extractant is most likely due to the removal of the extractant from the surfaces and pores of the membrane from the flowing aqueous phase. Shear forces may remove the extractant in the form of emulsions from the membrane to the aqueous phase as was illustrated in Figure 44. After a period of 4 days, a slight drop in the extraction efficiency of the Cr(VI) extractant impregnated membrane can be observed. This is possibly due to the occurrence of breakthrough. Cr(VI) trapped within the membrane may release previously extracted chromium from the membrane to the aqueous. This occurrence may be enhanced by the column flow, which is continuously pumped through the membrane.

5.5 *Column Extraction of Cr(III)/(VI) using Simulated Groundwater (SGW)*

The natural and anthropogenic sources of groundwater contamination have been described earlier. The interaction between groundwater and its environment regulate the migration of harmful substances from waste storage sites, landfills, *etc.* The importance of sampling groundwater for contaminants is essential to the maintenance of environmental, human & economic well-being. The application of this work to the separation, sampling, and preservation/stabilization of chromium species is dependent upon its performance not only in the laboratory-based experiments but also under conditions representative of the environmental application. Therefore, it was necessary to study the performance of these extractant impregnated membranes under conditions similar to those that would be encountered in the field. Therefore, the technique was investigated for its extraction efficiency under simulated groundwater conditions.

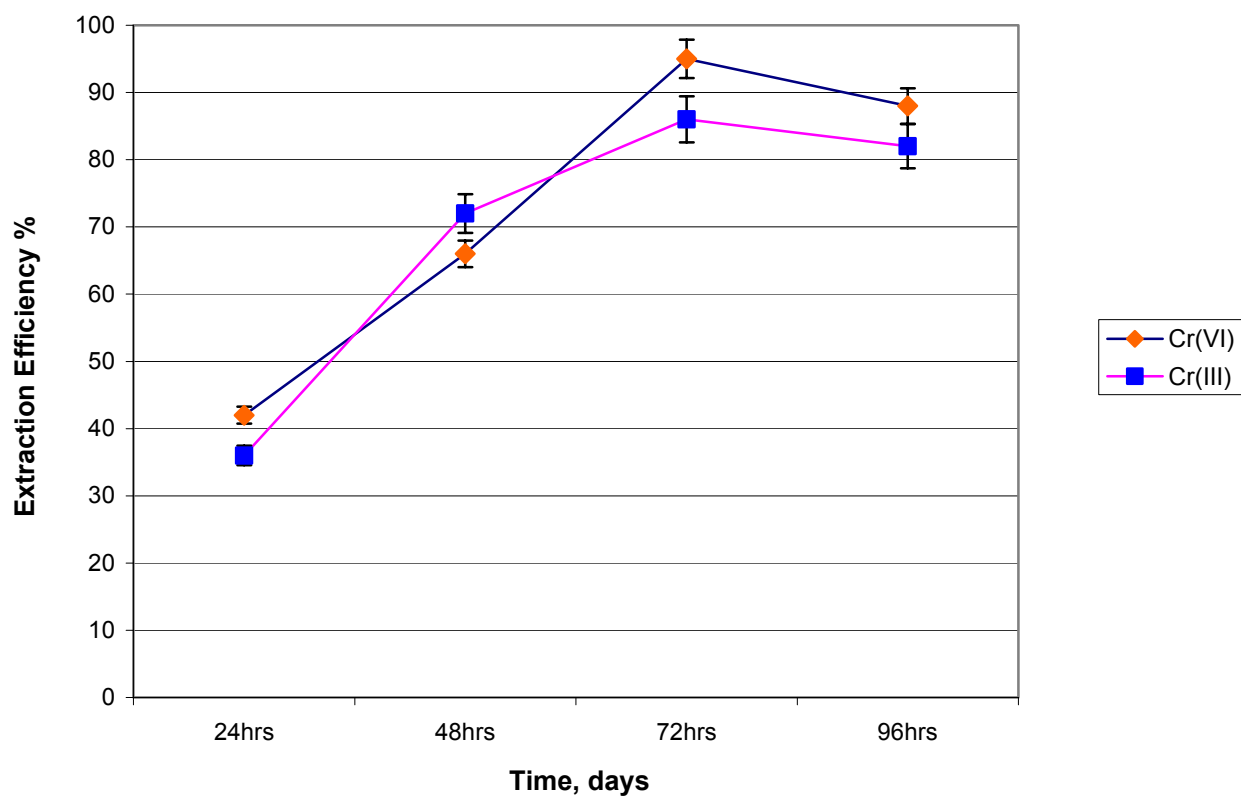


Figure 45. Extraction of Cr(III)/(VI) from Standard Solution using Column; source pH= 3.2, source phase composition 50 ppm Cr(III) and Cr(VI).

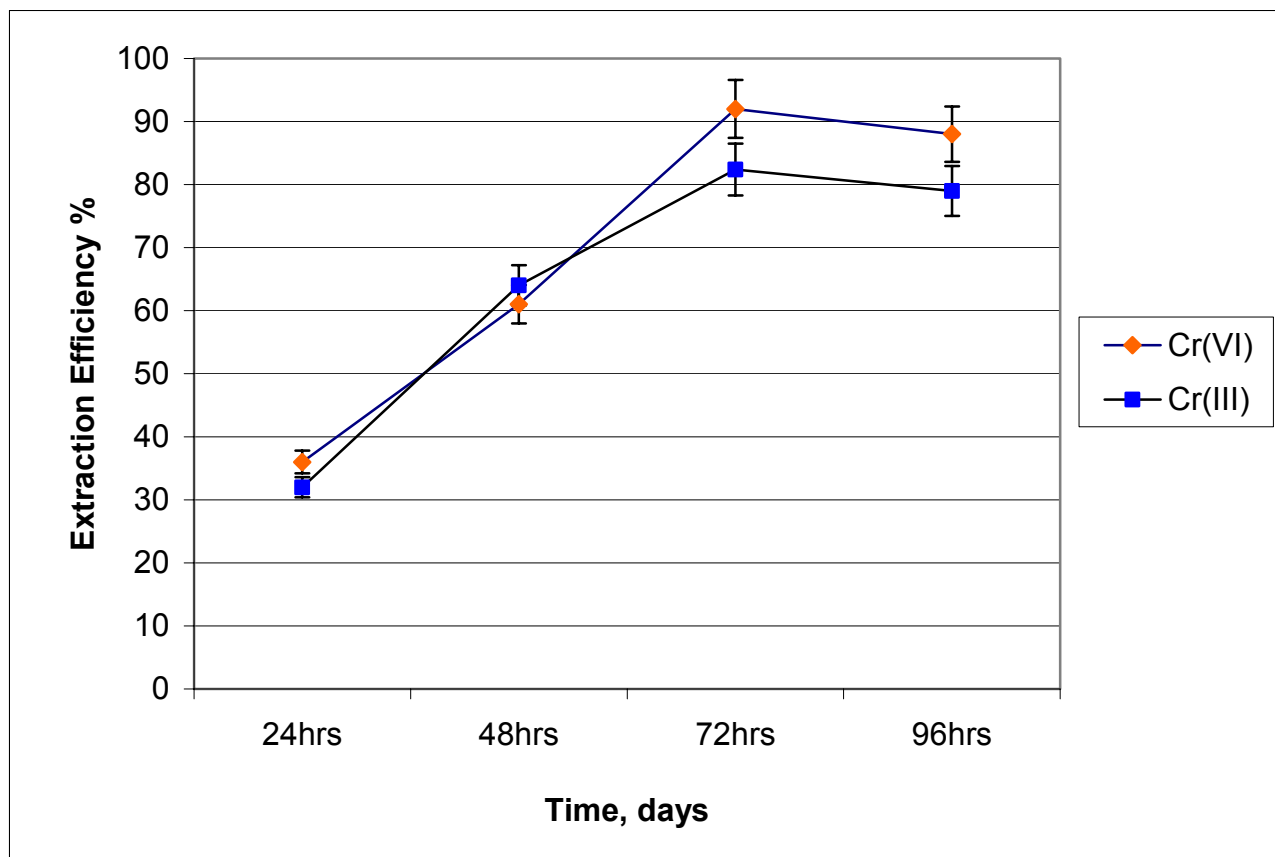


Figure 46. Extraction of Cr(III)/(VI) from Simulated Groundwater (SGW) using Column: source pH = 2.5, source phase composition 50 ppm Cr(III)/(VI).

Environmental matrices, such as contaminated groundwater, present a unique set of problems for analytical techniques due to the presence of interferents that would inhibit the performance of the technique. From the Table 9 the major cationic constituents of the simulated groundwater (SGW) used in this study are calcium and magnesium. A sufficient selectivity of DEHPA for Cr(III) over these cations would be required to obtain a satisfactory extraction efficiency of Cr(III) species. Similarly, a good selectivity for chromates over the anionic constituents of sulfate, chloride, and nitrate would be essential as observed in equilibrium investigations.

The extraction of Cr(III)/(VI) under simulated contaminated groundwater conditions is illustrated in Figure 46. As shown, there is a decrease in extraction efficiency over the period of 4 days as compared to the previous extraction of Cr(III)/(VI) in standard solution. This observed decrease in extraction efficiency is attributed to a number of factors. The presence of competitive ions in the groundwater solution is expected to decrease extraction efficiency to some level as observed in equilibrium investigations. As shown in equilibrium investigations, the presence of anionic constituents (chloride, sulfate and nitrate) in solution, decrease extraction efficiency to varying degrees. The presence of nitrate in concentrations of 0.001M-1 M during equilibrium investigations was shown to inhibit Cr(VI) extraction. Concentrations of 0.030 M nitrate in the simulated groundwater used in this study is suspected to decrease Cr(VI) extraction to some degree.

The decreased extraction efficiency of Cr(III) under simulated groundwater conditions is also attributed to the presence of competitive ions. DEHPA is an excellent extractant for the removal of divalent and trivalent cations in a wide range of operating conditions, due to its chemical stability, high selectivity for metal species [38] and extremely low aqueous solubility. The extraction of Cr(III) species also exhibits slower extraction kinetics after a period of 2 days. This is possibly due to the fact that DEHPA is not wholly controlled by complex formation reactions at the aqueous-organic interface,

but more or less by diffusion of the metal complex in the organic stagnant layer, or by diffusion of metal ions in the aqueous stagnant layer [38].

Aside from cationic and anionic interferences that would inhibit Cr(III)/(VI) extraction, contaminated wastewaters and groundwaters originating from hazardous waste sites introduce the additional problem of lowered pH values versus natural waters which lie in the pH range of 4-7. The pH of the environmental system is dependent upon soil composition and texture, contaminant, location, *etc.* Of particular interest, is the effect of soil matrix on the pH of the environmental system, which in turn affects the concentration of contaminants in groundwater. The affinity of contaminants to different soil components, at different pH levels, and their mobility with respect to various geometric processes are illustrated in Table 16.

The investigation concerning contaminated simulated groundwater was accomplished using seasand to mimic an acid sandy matrix of pH values ranging from 2.5-4. This acid sandy soil matrix was chosen due to the fact that it presented a set of challenges that would test the limits of the sampling technique. At the pH values 2.5-4, there exists higher mobility of contaminants in the subsurface groundwater due to the lowered pH values. Oxidation-reduction reactions of chromium species are well-demonstrated at lowered pH values and therefore would present another set of challenges. Extraction of Cr(III)/(VI) with DEHPA and Aliquat-336 has already been shown to be dependent on pH. The performance of DEHPA and Aliquat-336 under extreme conditions of high contaminant mobility and lowered pH would be of interest in this study. The advantage of investigating the acid sandy medium as the matrix of choice is

Table 16. Various pH Values of Trace Elements in Groundwater with respect to Soil Matrix. Reproduced from [62]

Element (ppm)	Acid sandy (2.5-4)	Sandy (4-4.5)	Silty (5.5-6)	Loamy (7-7.5)	Calcareous (7.5-7.8)
Cd	107	nd	nd	nd	nd
Cu	783	76	20	50	50
Mn	5695	8000	5000	100	700
Pb	5999	nd	nd	nd	nd
Zn	7137	1000	5000	100	300
Co	nd	nd	nd	0.5	5

also due to the fact that the main focus of the experiment is to study the performance of the sampling system and not the adsorption characteristics of the matrix (*i.e.* humic acids, Al/Mn oxides, clay minerals), which retain metal ions. Removal of chromium species from the source solution should be attributed only to the extractive capabilities of the sampling system. The acid sandy matrix reflects little to no interference to the extraction of metal ions from solution. Thus, extraction of chromium ions from the source solution can only be attributed to the sampling system and not the soil matrix.

In an effort to study the extraction efficiency of the technique under contaminated groundwater conditions in an acid sandy matrix, the source phase was adjusted with H₂SO₄ to a pH of 2.5. In Cr(VI) extraction at pH values below 2, extraction efficiency decreases possibly due to an increase in protons concentration in the feed solution that forms species like H₂Cr₂O₇ or HCr₂O₇, which may not ionize completely at high acid concentration to form a complex with the Aliquat cation [26]. Thus, extraction of Cr(VI) ions will decrease. Additionally, Cr(VI) is reduced to Cr(III) in acidic conditions and the rate of reduction increases with decreasing pH [20]. In Cr(III) extraction at pH values below 2, a decrease in extraction efficiency is observed, which more than likely due to proton competition with cationic Cr(III) for DEHPA [23] (Figure 29). Additionally, at low pH values less DEHPA ion exchanger is available, DEHPA has been protonated [16]. Therefore, extraction efficiency would be expected to decrease.

A t-test was used to determine if the analyte recovery produced by the column studies differed significantly from those produced by batch experiments. The null hypothesis (H₀) was established that there was no significant difference in the column analyte recoveries versus batch recoveries. The appropriate t-test equation used was

$$t = \frac{(\bar{x} - \bar{x})}{\sqrt{(s_1^2/n_1 + s_2^2/n_2)}}$$

where \bar{x}_1 and \bar{x}_2 are the means for data sets 1 and 2, respectively, and s_1 and s_2 are the corresponding standard deviations. The calculated t-value was compared to a table value at 95% confidence level, according to the appropriate number of degrees of freedom. H₀

was then accepted ($t_{\text{calc}} < t_{\text{table}}$) or rejected ($t_{\text{calc}} > t_{\text{table}}$), based upon this comparison. Results from the t-test showed are shown in Table 17. There is not a statistical difference between the column Cr(VI) recoveries versus the batch Cr(VI) recoveries. Performance of the column extraction efficiency is comparable to those obtained in batch experiments for Cr(VI) extraction. Cr(III) recoveries obtained from the column experiments, however, show a statistical difference from those obtained from batch experiments.

5.6 *Summary*

The extraction efficiency of the extractant impregnated membranes when incorporated into the column assembly was an essential portion of this work. Equilibrium investigations have already illustrated the excellent performance of the sampler under batch conditions. Previous studies in this work illustrate that the extraction efficiency of the system is demonstrated upon several factors, including work extractant concentration, choice of stripping agent and concentration, presence of interfering cations/anions, pH, and ionic strength. The stability of the sampling system when incorporated into the column shows a slight decrease in extractant loss from the membrane. This loss was primarily attributed to the flow induced through the membrane which may subsequently enhance extractant loss versus studies conducted in batch when extractant loss was studies at equilibrium (no flow/stirring speed).

The extraction efficiency of the column sampling system when run with chromium standard solutions showed sufficient extraction of approximately 95% Cr(VI) and 88% Cr(III). Again, loss of extractant is the main factor being attributed to the observed decrease in extraction efficiency from 100% shown in equilibrium investigations. The performance of the column sampling system was further tested through the use of a simulated contaminated groundwater source solution. The acid sandy matrix provided an excellent choice of medium under which to study the extraction capabilities of the system under extreme conditions of lowered pH and high contaminant mobility. The acid sandy medium allows the performance of the sampling system to be

Table 17. t-test Comparison of Column Analyte Recovery vs. Batch Analyte Recovery

$$H_0: x_1 = x_2$$

(no significant difference between column and batch recoveries)

Data Set #1		Data Set #2	
<u>Column Cr(VI) Recoveries</u>		<u>Batch Cr(VI) Recoveries</u>	
	93		100
	88		100
	92		100
Mean (x)	91		100
Std. Dev	2.65		0

$$t_{\text{calc}} = 1.965$$

$$t_{\text{table}} = 2.353 \text{ (one-tail comparison)}$$

Therefore, since $t_{\text{calc}} < t_{\text{table}}$, accept H_0

There is no statistical difference between the column Cr(VI) recoveries versus batch Cr(VI) recoveries

<u>Column Cr(III) Recoveries</u>		<u>Batch Cr(III) Recoveries</u>	
	84		100
	80		100
	82		100
Mean (x)	82		100
Std. Dev	2		0

$$t_{\text{calc}} = 2.601$$

$$t_{\text{table}} = 2.353 \text{ (one-tail comparison)}$$

Therefore, since $t_{\text{calc}} > t_{\text{table}}$, reject H_0

There is a statistical difference between the column Cr(III) recoveries versus batch Cr(III) recoveries

studied without interferences to the extractive capabilities of the system due to possible adsorption characteristics of the matrix (*i.e.* humic acids, Al/Mn oxides, clay minerals), which retain metal ions.

Extraction efficiency of the column sampling system was subject to a slight decrease in extraction efficiency as compared to batch experiments. This was attributed to the lowered pH. Results from t-tests show that Cr(VI) extraction using the column is not statistically different from those obtained in batch experiments. Thus, performance of the column is comparable to the excellent extraction efficiencies observed with batch experiments. On the hand, t-tests on Cr(III) extraction using the column revealed a statistical difference between the column Cr(III) recoveries and those from batch Cr(III) recoveries. This is attributed to the lowered pH of the simulated contaminated groundwater. Cr(III) extraction at pH values below ~2, illustrate a decrease in extraction efficiency, which is more than likely due to proton competition with cationic Cr(III) for DEHPA. Additionally, at low pH values less DEHPA ion exchanger is available due to the fact that DEHPA has been protonated.

The extreme conditions under which the simulated contaminated groundwater column studies were performed illustrate the stability and performance of the sampling system at the most extreme conditions. At lowered pH values, oxidation-reduction reactions are presenting a more complex situation for chromium species, chromium(III)/(VI) extraction is hindered by cationic/anionic interferences present in groundwater, increased contaminant mobility is expected under highly acidic conditions, and the behavior of the selected extractants are altered at lowered pH levels. All of these factors taken into account, the extraction efficiency of Cr(VI)/(III) species remains to be sufficient, but does suffer a slight decrease in Cr(III) extraction efficiency from those observed in equilibrium investigations due to the factors discussed previously.

Chapter 6

6. Conclusions

The increasing concern towards the removal of transition metal ions from industrial wastewaters and groundwater requires the development of advanced separation systems. Through the need for more specific systems, new ion exchange resins, solid adsorbents and metal extractants used in solvent extraction processes have been developed for different applications. This work centered on the application of extractant impregnated polymers for the *in-situ* sampling, separation/removal, and stabilization of chromium species. In this approach, the extractant molecules were adsorbed onto a polymeric support to produce an extractant impregnated polymer. Extractant impregnated polymers maintained the specificity of the metal extractants used in liquid-liquid extraction systems and while avoiding chemical functionalization of the polymeric support. The principles of solvent extraction, ion exchange and supported liquid membranes all form the basis for extractant impregnated membranes. Extractant impregnated polymers possess the advantages of liquid-liquid extraction including the great variety of ion exchangers (widening the range of applications) and the simplicity of solid ion exchange.

The application of extractant impregnated membrane technology offers considerable advantages over solvent extraction, ion exchange and supported liquid membranes. The major drawback of solvent extraction is the dispersion of the solvent, which has both environmental and economic implications. Ion exchange has the disadvantages of a limited range of possible applications, compared with reactive extraction. The choice of a suitable ion exchange resin is also often difficult, since the resins can be either high loaded or they have a high selectivity. Supported liquid membranes hold the promise of high performance with a minimal amount of extractant. This presents an advantage over solvent extraction. One weakness of supported liquid membranes is the loss of extractant to the aqueous phase, which has a profound effect on the lifetime of the system. Extractant impregnated membranes avoid the problems plaguing these extraction methods.

The extractants commonly used in extractant impregnated membranes are generally those employed in solvent extraction. The quaternary ammonium salt, Aliquat- 336 has been extensively used in solvent extraction and has been shown in this study to be a very efficient extractant in the removal of Cr(VI) anions. The acidic organophosphorus extractant, DEHPA, has been widely studied in the past and has been shown to be an effective extractant for transition metals and lanthanides. DEHPA was shown to be an effective extractant of Cr(III) with nearly complete extraction during batch experiments. The stability of chromium standard solutions was investigated to observe the contribution of interconversion and degradation processes occurring. Cr(III) and Cr(VI) standard solutions were found to be stable for at most 30 days. Optimal storage conditions for chromium standard solutions were determined to be storage of chromium solutions in polyethylene bottles at 4°C for a maximum of 30 days to avoid degradation and interconversion of chromium species.

Extractant impregnated membranes were proven to be an efficient separation technique for the preservation and stabilization of chromium species during batch experiments. Optimal extraction conditions for Cr(VI) were found to be an extraction time of at least 5 days, source phase pH between 3-5, an extractant concentration of 1 v/v% Aliquat-336, and 1 M NaOH as stripping agent. Optimum conditions for Cr(III) extraction using DEHPA are extraction time of at least 5 days, source phase pH between 3-5, an extractant concentration of 30 v/v% DEHPA, and 0.5M HNO₃ as stripping agent. Stripping of the impregnated membranes was investigated to observe the regeneration capability of the sampling technology. Stripping of Cr(VI) from the Aliquat-336 impregnated membrane with 1M NaOH yielded almost complete removal of the extracted species from the membrane. A residual 2-4% was calculated to remain in the membrane. Stripping of Cr(III) from the DEHPA impregnated membrane with 0.5 M NaOH removed approximately 95% +/- 3 of the extracted species from the membrane with a residual 5-8% remaining in the membrane. Batch studies employing extractant impregnated membranes show that the technique is affected by the presence of interferences (both cationic and anionic). The nitrate anion poses the greatest interference to Cr(VI) extraction due to its affinity for Aliquat-336. The cations Al³⁺ and Fe³⁺ pose the greatest interference to Cr(III) extraction due to their similar chemistry to Cr(III) and their close association to Cr(III) in the environment.

Surface analysis yielded important information on the nature of the membranes and visual evidence of the extractant presence on the surface and in the pores of the membrane. Scanning electron microscopy produced information on the surface and subsurface morphology of the polymeric membranes and visibly showed evidence of the extractant in the pores and on the surface. X-ray photoelectron spectroscopy revealed elemental composition changes in the surface of the membrane due to the process of impregnation and offered evidence of extractant presence on the surface of the membrane. To confirm coverage of the extractants onto the polymeric membranes, the elemental percentages obtained by XPS were compared to the atomic percentages calculated from the molecular structure of each extractant (Aliquat and DEHPA). The results showed that virtually complete coverage was obtained in the impregnation of Aliquat and DEHPA on both the Versapor and WPP membranes.

Membrane stability studies demonstrated the lifetime of these membranes under varying conditions (equilibrium and under induced stirring speed). The “dry surface membrane impregnation” technique proved to be a more efficient preparation method in comparison to the “wet surface membrane” technique. The dry surface method of impregnation resulted in reduced loss of the extractant to the aqueous phase. This reduction in membrane loss was attributed to the decrease in emulsion formation, which is often a problem plaguing wet surface membranes. Emulsion formation has been found to be a primary cause of membrane instability and decreased lifetime of the prepared impregnated membrane techniques. Linear flow velocity was shown to increase loss of extractant from the membrane phase during batch and column experiments.

Column extraction efficiency under simulated groundwater conditions was dependent upon pH. The pH values of contaminated wastewaters and groundwaters originating from hazardous waste sites are reportedly lower (pH values of 2-3) than those of unpolluted natural waters (pH values of 4-7) with reportedly higher concentrations of contaminants (5-200 ppm). Lowered pH conditions introduce an additional area of concern in that extraction efficiency of the technique is dependent on pH. At lowered pH conditions Cr(VI) species are susceptible to reduction to Cr(III) and an increase in protons concentration in the feed solution may form species like $\text{H}_2\text{Cr}_2\text{O}_7$ or HCr_2O_7 , which may not ionize completely at high acid concentration to form a complex with the Aliquat cation. At pH values below 2, a decrease in extraction

efficiency of Cr(III) may occur due to proton competition with cationic Cr(III) for DEHPA. Additionally, at low pHs less DEHPA ion exchanger is available, due to the fact that DEHPA has been protonated. Thus, extraction efficiency decreases. Column studies were performed at a pH value of 2.5 and the extraction efficiency of Cr(VI) was found to be not significantly different from those obtained in batch experiments. Column studies of Cr(III) extraction showed, however, that recoveries are significantly different from those obtained in batch. The source of decreased extraction efficiency was attributed to less ion exchanger available due to DEHPA protonation.

The impregnation of a polymeric support by an extractant is a straightforward and simple procedure. The separation of analytes on impregnated membranes incorporated into a multiplayer sampling device is a very attractive method for the separation and preservation of chromium species. There are many applications for the use of extractant impregnated membranes incorporated into a sampling device such as the one designed. The selective ion trap allows several units to be incorporated within the same column if needed. Groundwater at various points within an aquifer at various depths may be sampled eliminating the necessity for multiple samplers. Also, these extractant impregnated membranes may be tailored to extract different analytes of interest (such as mercury, lead, arsenic etc.), which also exhibit complex chemistry and speciation.

Aside from the application presented in this work regarding metal speciation in contaminated waters, extractant impregnated membranes could also find use in the purification of water and metal solutions. The developed knowledge can be applied to the decontamination of radioactive wastes. The technique can assist in developing models for predicting the bioavailability of metals from biological systems, modeling of biological membranes, and drug delivery. The principle of extractant impregnated membranes may also be applied to ion selective electrodes, which generally consist of either solid ion exchanger or a liquid ion exchanger as ion sensors, and are entrapped in a neutral carrier such as polyvinylchloride. The analytical technique presented could be an excellent method for sample clean-up of complex matrices. Enrichment of valuable metals, such as gold and silver, is another application in which the technique may be used.

The potential impacts of this project on advancing knowledge in the area of science are far-reaching. This study presents the process of how sampling and storage should be handled to obtain accurate results in regards to chromium speciation, which is an area requiring more study. Additionally, the technique presented allows an accurate representation of the sample taken at the point of collection, which is often a problem plaguing chromium sampling and storage. As a result, hazards of chromium-bearing wastes will be accurately evaluated. This study avoids problems associated with stabilization and preservation of individual fractions of chromium species in solution. In contrast to existing methods that have severe stability, economic, and technical problems.

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