ION CHROMATOGRAPHY OF SOLUBLE

Cr(III) AND Cr(VI)

THESIS

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Ion chromatography coupled with a conductivity detector was used to investigate the analysis of Cr(III) and Cr(VI) in aqueous samples. An IC methodology for Cr(III) was developed using a cation column and an eluent containing tartaric acid, ethylenediamine, and acetonitrile at pH 2.9. The detection limit of this method can reach 0.1 ppm level with good precision. Several operational parameters were evaluated during the regular use of the method. Comparison of the IC method with AA method showed good agreement between the two methods.

The anion exchange column was used for Cr(VI) determination. The best results were obtained with an eluent containing sodium gluconate, borate buffer, glycerin, and acetonitrile. The retention time for the Cr$_2$O$_7^{2-}$ sample was 11 min. and the calibration curve was linear between 1.0 and 100 ppm.
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CHAPTER I
INTRODUCTION

The purpose of this research was to develop and evaluate ion chromatographic methodologies for the analysis of Cr(III) and Cr(VI) in natural water systems.

This chapter includes a literature review on ion chromatography of transition metals and the aquatic chemistry of chromium.

Ion Chromatography of Transition Metals

The term ion chromatography was introduced by Small, Stevens, and Bauman in 1975 (1), to describe liquid chromatography (LC) determination of ions by separation on a low capacity ion-exchange column followed by conductivity detection of the solute species. Sensitivity of detection was enhanced by passing the effluent containing the separated ions through an eluent modification device (commonly called a suppressor) that chemically modified the eluent to reduce its conductivity (2).

In 1979, Fritz and co-workers demonstrated that, by using eluents that already displayed low conductivity, the suppressor device was not necessary for the high sensitivity
determination of ions (3). In a continuation of this work, Fritz described a variety of organic acid eluents that could be successfully employed for high sensitivity determination of ionic species (4). This was an important development, because suppression devices were expensive, complex, and severely limited the development of chromatographic procedures. By restricting the use of mobile phases to those compatible with a suppressor, chromatographers were unable to select the optimum eluent composition for separation.

Due to the strong affinity of transition metal ions for the cation exchange site of the stationary phase, eluents of high ionic or acid strength are normally required for elution of metals. Suppressed cation IC, however, is not compatible with transition metal determination because the insoluble hydroxides of the metals are formed in the suppressor.

High-performance liquid chromatography (HPLC), thin-layer chromatography (TLC) and gas chromatography (GC) also have been used for transition metal analysis. Many earlier applications of HPLC (5), TLC (6), and GC (7) were limited to the separation of metal complexes or chelates rather than the "free" transition metal ions. These methods typically require solvent-extraction. In 1953, Kraus and Moore (8) demonstrated the usefulness of ion exchange chromatography for the separation of transition metals.
Ion chromatography is now a very useful alternative analytical tool for the separation and detection of both free transition metal ions and metal complexes (9, 10, 11). To understand the mechanism of separation, consider a strong cation-exchange resin to be used for the separation of two transition metal ions, $A^{n+}$ and $B^{n+}$. When an eluent containing monovalent cations such as $Na^+$ or $H_3O^+$ is used, the two metal ions often show similar chromatographic behavior and thus coelute. For metal ions with similar charge-to-size ratios, their chromatographic separation by pure cation exchange under equilibrium conditions is very difficult. By employing an eluent that contains complexing agents (ligands or chelating agents), the ion-exchange properties of the metal ions can be radically altered. Choosing complexing agents for which the formation constants of different metal ion complexes are significantly different allows for rapid and complete separation of most metal ions. The competing equilibria of complex ion formation in the ion-exchange process allows for a wide variety of separations of metal ions using anion- and cation-exchange resins.

The ion-exchange behavior of a metal ion complex is primarily dependent on the charge of the complex. In general, the greater the difference in the charge of the metal ion and metal ion complex, the more effective the chromatographic separation. If the eluent contains neutral
complexing agents (eg., ammonia or ethylenediamine), the charge of the metal ion will not change when complexed. This type of complexation does not significantly affect the exchange selectivity.

If complexation with a charged ligand or chelating agent results in a neutral complex, a dramatic change occurs in the exchange equilibrium. The metal ion is now bound in the neutral complex, which cannot be ion exchanged or retained by the chromatographic packing (12). If complexation continues another step to a complexing anion, the positively charged metal ion is now bound in an anionic complex and the ion-exchange equilibrium is again radically altered. Because stoichiometry of the metal ion complex will depend upon the metal, oxidation state, complexing agent, and pH, the resulting complex ion-formation and ion-exchange equilibria can only be approximated in theoretical calculations.

With low-capacity pellicular ion-exchange resins, the complexing agents which offer the maximum separation of metal ions are weak organic acids. Acids such as tartaric, citric, oxalic, and phthalic have been used as moderate strength chelating agents in ion-exchange separations. In 1983, Sevenich and Fritz (11) used a conductivity detector in ion chromatography in conjunction with a complexing eluent. In their work eluents containing the ethylenediammonium cation and either tartrate or
hydroxyisobutyrate as the complexing anion were used for separation of transition metals. The use of a complexing agent in the eluent improves the sharpness of separation and broadens the scope of cation chromatography with a conductivity detector.

A coulometric detector was developed by Takata and Fujita (13) to study the rapid separation of heavy metal ions by cation-exchange chromatography using sodium tartrate solution as the eluent. Girard (14) modified the detection system by using primary and secondary controlled-potential coulometry, which extended the capabilities of the ion chromatography technique to the analyses of alkali and alkaline earths, rare earths, and transition metals. Later Cassidy and Elchuk (15) interfaced a post-column reactor to the high-performance chromatograph; 4-(2-pyridylazo) resorcinol monosodium salt (PAR) was used as the color-forming reagent, and with spectrophotometric detection at 540 nm most metal ions could be determined in the ng ml\(^{-1}\) and pg ml\(^{-1}\) ranges. In 1983, Sevenich and Fritz (11) developed a single-column method that used a conductivity detector and a complexing agent. This technique not only provided a rapid and highly selective method for separating and determining magnesium, calcium and strontium but also extended the application of conductivity detection to divalent metal ions and the trivalent lanthanide cations.
Mobile Phases of Transition Metals
in Ion Chromatography

Ion exchange involves an exchange of ions between the mobile phase and the stationary phase. This means that a buffer ion must be liberated whenever a sample ion is bound to the stationary phase and vice versa. In turn, it means that the concentration of ions in the column effluent remains constant; only the identity of the ions changes. When electrical conductivity detection is coupled with ion exchange separation, detection sensitivity depends on the difference in equivalent conductance between buffer and sample ions. One can visualize a situation in which buffer and sample ions are similar in equivalent conductance. The result would be poor sensitivity because the conductivity changes only slightly as sample ions replace buffer ions.

The chemical suppression approach to IC developed by Small, Stevens, and Baumann in the 1970s improved sensitivity by passing the column effluent that was sodium carbonate-sodium bicarbonate solution through a suppressor column (1). The result was the conversion of sodium carbonate (high-equivalent conductance) into carbonic acid (low-equivalent conductance). When sample ions (chloride, for instance) emerge from the column, they are converted into high-equivalent conductance hydrochloric acid, respectively. The net effect is to amplify differences in
equivalent conductance.

Chemical suppression does improve sensitivity, but introduces its own set of problems (16): it adds complexity (and cost) to an otherwise simple system; it adds dead volume (and band spreading) to the system between the separator column and the detector; and it is limited to strongly dissociated sample ions. As mentioned before, suppressed cation IC is not compatible with transition metal determination because the insoluble hydroxides of the metals are formed in the suppressor.

A single-column ion chromatography (SCIC) using conductivity detection was developed during the late 1970s by Fritz et al. (3, 12, 17) in response to some of the disadvantages of chemical suppression IC. The key to the development of SCIC was the observation that differences in equivalent conductance determine sensitivity. SCIC using conductivity detection simply relies on the choice of an eluent buffer whose equivalent conductance differs greatly from that of the sample ions.

The first rule for eluent selection in SCIC with conductivity detection then is: wherever possible, choose an eluent buffer which maximizes the difference in equivalent conductance between the sample and the buffer (18). Because sample ions are likely to be intermediate in equivalent conductance, the most generally useful buffer ions have either very high or very low-equivalent conductance. In
anion analysis, this usually means big, bulky organic acids or their salts (low-equivalent conductance) or hydroxide ion (high-equivalent conductance). Most cation separations are carried out using high-equivalent conductance-driving ions such as hydronium (monovalent) or ethylenediammonium (divalent).

In order to effectively optimize anion exchange separation in single-column ion chromatography, several factors must be considered. Determination of eluent-driving strength is one of the factors. In general, the driving strength of a buffer ion is closely related to its affinity for the ion exchanger used. Other thing being equal, the order of affinity/driving strength is monovalent < divalent < trivalent. A great deal of flexibility in system optimization is available, therefore, if one choose a buffer ion which is a divalent (or trivalent) weak acid with different pK_a values for each ionization. This allows the relative concentration of monovalent (weak) and divalent (strong) driving ions to be controlled by changing pH. It will be demonstrated shortly that a greater interaction (adsorption) of the eluent anion with the resin structure also tend to increase the effectiveness of an eluent to eluate sample anions (4). The selectivity coefficient of the ion-exchange resin for the eluent anion is also an important factor in determining the ability of an eluent to eluate sample anions.
The most common eluents for anion analysis in SCIC are based on organic acids and their salts (3, 17, 19, 20). Most frequently used have been the sodium or potassium salts of benzoic acid, hydroxybenzoic acid, or phthalic acid. These eluents have a strong enough affinity for the anion exchange resins while also having low molar conductivities. Most sample anions have a higher equivalent conductance than that of the eluent anions and can therefore be detected even when present in concentrations in the low part per million range. When using aromatic acids as eluents, the pH of the solution must be adjusted to between 4 and 7; since the pH determines the degree of dissociation of these acids and, thus, the retention behavior of species being analyzed (21).

Using aromatic carboxylic acids as eluent, the separation of inorganic anions is possible. Sodium or potassium benzoate is preferred for separation of monovalent anions. For eluting divalent species, the corresponding salts of phthalic acid have to be used since these salts have a stronger affinity for the stationary phase. Increasing the concentration of benzoate is not possible due to the resulting, higher conductivity making sensitive conductivity detection impossible.

The most commonly encountered approach to SCIC analysis of monovalent cations uses a dilute mineral acid buffer (typically 1-10 mM nitric acid) (12). However, divalent sample ions are generally too strongly retained to be eluted.
by a monovalent driving ion such as the hydronium. The analysis of divalent cations is typically carried out using a high-equivalent conductance divalent driving ion such as ethylenediammonium. Because both of these eluents are more highly conducting than the sample cations, the sample peak are negative relative to the background (decreasing conductivity). The difference in equivalent conductance between the eluent and sample cations is quite large, and the detection sensitivtiy is very good, particularly with the acidic eluent.

Due to the strong affinity of transition metal ions for the cation exchange site of the stationary phase, a complexing eluent is normally required in order to reduce its charge density. Thus, monovalent cations, such as Na⁺ or H⁺ are not suitable as eluents. Since the selectivity coefficients for transition metal complexes having the same charge are essentially the same, changes in selectivity with respect to a cation exchange column can only be achieved via the formation of neutral or anionic complexes during the separation by employing appropriate agents. Typical complexing agents are the weak organic acids which preferentially form anionic complexes with transition metals, i.e., citric acid, oxalic acid, and tartaric acid. The results of separations using these acids are considerably better than those obtained with compounds that form cationic complexes, such as ammonium hydroxide and
ethylenediamine. An optimum separation can be obtained if a mixture of two different complex forming acids are used as eluents.

Because weak organic acids are effective chelating agents only when ionized, eluent pH has a dramatic effect on the separation and retention of the metal ions (22). In cation exchange, an increase in the eluent pH to the pKa of the acid will result in a decrease in the retention time of the metal ion. This occurs because the increase in pH results in an increase in the concentration of the chelating form of the acid. Thus, the residence time of the metal ion in the eluent increase due to enhanced complexation. This shifts the equilibrium of the metal ion from the stationary phase (resin) to the mobile phase (complexing eluent), thus, decreasing retention. The exchange equilibrium can be altered by a change in the eluent concentration or by a change in the eluent pH.

In summary, transition metal ions are generally too strongly retained to be eluted by monovalent driving ion such as hydronium. A complexing eluent is normally required in order to reduce its charge density. Typical complexing agents are citric acid, oxalic acid, tartaric acid, and ethylenediamine. Eluents containing the ethylenediammonium cation and either tartrate or hydroxyisobutyrate as the complexing anion have been used (11, 23). The use of a complexing agent in the eluent improves the degree of
separation. In recent work, ethylenediaminetetraacetate (EDTA) has been used to separate transition metals such as $\text{Zn}^{2+}$, $\text{Mn}^{2+}$, $\text{Cu}^{2+}$, $\text{Fe}^{2+}$, and $\text{Ni}^{2+}$ (24). Because the complexing agent has weak absorbance, both UV detector and conductivity detector can be applied.

Ion chromatography, a once narrowly defined conductivity-based technique, is emerging as an indispensable analytical tool. A multitude of ionic species can now be determined quickly, simply, and at high levels of sensitivity with ion chromatography. Modern ion chromatography can now be used to determine not only most of the transition metals, but also inorganic anions, cations, organic acids, amino acid, and peptides simply by correctly selecting the proper polymeric column, mobile phase, and detector.

Stationary Phases of Transition Metals in Ion Chromatography

Many substances including clays, natural and synthetic zeolites, certain glasses, some inorganic oxides and insoluble salts, and functionalized organic polymers, have the ability to exchange one ion for another. By far the most important in ion-exchange chromatography are ion exchangers made from organic polymers such as styrene-divinylbenzene copolymers or a porous silica or other support to which has been grafted or chemically coated an
ion-exchanger material. Ion-exchange materials may be classified as cation exchangers or anion exchangers.

Anion-exchange resins are prepared by chloromethylating the benzene rings in styrene-divinylbenzene copolymer and then alkylating by reaction with an aliphatic amine. The most common type of anion-exchange resin contains a quaternary ammonium functional group, obtained by alkylation with trimethylamine (25).

\[
\begin{align*}
\text{Res} & \xrightarrow{\text{ClCH}_2\text{OCH}_3, \text{ZnCl}_2} \text{Res} \quad \text{N(CH}_3)_3 \\
\text{Res} & \quad \text{CH}_2\text{Cl} \\
\text{Res} & \quad \text{CH}_2\text{N(CH}_3)_3\text{Cl}^-
\end{align*}
\]

In these resins only the anion is mobile and can be exchanged for another anion.

Polymeric resins are being used more frequently in modern liquid chromatography applications as improvements in polymeric packing materials are realized and as more applications are developed for these materials. Use of modern polymers has overcome earlier problems associated with their use; higher rigidity now allows them to be used at normal eluent flow rates resulting in faster analyses, and improved synthesis techniques have resulted in
efficiencies comparable to the best silica materials (26). In addition, polymeric resins are unaffected by the pH of mobile phases; many polymers are stable from pH 0 to 14.

Although silica-based ion exchangers can give excellent separation, they should not be used in conjunction with eluents that are very basic, because at pH above 7.0 severe degradation of the resin occurs. Thus, silica-based resin column lifetimes are short.

For anion IC, a binary pellicular resin is used in the separator column as in Fig. 1(A) (22). As in the case of the cation separator resin, the core of the resin particle is polystyrene-divinylbenzene. Surrounding this core is a layer of sulfonated polystyrene-divinylbenzene. The purpose of the sulfonated layer in this resin is to provide a surface to which the outer anion exchange layer is bound via ionic bonding interactions. The outer layer consists of uniformly sized anion-exchange latex particles which are deposited on the sulfonated layer in a uniform monolayer.

For cation IC, the separator resin is surface sulfonated ion-exchange resin as in Fig. 1(B) or a binary pellicular resin with cation exchangers attached to the surface of the resin spheres, analogous to the anion exchange particles in Fig. 1(A). The inert polystyrene-divinylbenzene core of the resin particle provides a rigid support for the sulfonated outer layer. Unlike high capacity ion-exchange resins, this type of material does not
Figure 1  (A). Composition of the IC anion-exchange particle.  
(B). Composition of the IC cation-exchange particle.  
(from reference 22)
change size appreciably when converted from one cation to another.

The exchange capacity of a resin can be varied by using short reaction times and very mild conditions for the chemical reaction that introduces the functional group (22). For cation-exchange resins it has been shown that the distribution ratio of a metal cation decreases substantially with decreasing resin exchange capacity. For anion-exchange, the selectivity coefficient was found to remain constant as the resin capacity was varied. This agrees with expected exchange behavior and has important implications for ion-exchange chromatography.

Consider the exchange equilibrium for ions A and B on an ion-exchange resin (22).

\[ A^{a+} + B^{b+r} \rightleftharpoons A^{a+r} + B^{b+} \]  

(1.1)

In general, the selectivity coefficient \( K_c \) is expressed as:

\[ K_c = \frac{[A^{a+}]_r [B^{b+}]}{[A^{a+}] [B^{b+r}]_r} \]  

(1.2)

where \([A] : \) the concentration of analyte ion in the mobile phase

\([A]_r: \) the concentration of analyte ion in the resin phase

\(a : \) the valency of analyte ion
[B] : the concentration of eluent ion in the mobile phase

[B]r: the concentration of eluent ion in the resin phase

b : the valency of eluent ion

The distribution coefficient D for an ion exchange separation is given by

\[ D = \frac{K_c^{a/b} [B]^a}{[B]^b} \]  

The distribution coefficient is related to a more readily determined chromatographic parameter, the capacity of factor \( k' \):

\[ k' = \frac{D V_m}{V_s} = \frac{(K_c)^{a/b} [B]^a V_m}{[B]^b V_s} = \frac{t_1 - t_0}{t_0} \]  

where  \( V_m \): the volume of the mobile phase in the column

\( V_s \): the volume of the stationary phase

\( t_1 \): the retention time of the analyte ion

\( t_0 \): the retention time of an unretained peak

In general the affinity of an ion exchanger for an ion increases with the charge on the ion, e.g., trivalent ions are preferred over divalent ions, and divalent ions over monovalent ions. For different ions of the same charge, the larger the ionic radius, the more strongly they are
attracted to an ion exchange site.

For both anion and cation exchangers, the resins used were low capacity in order to minimize the concentration of the buffer eluent employed as the mobile phase. High capacity of the resin will require high concentration of the eluent to push the sample ion from the resin site which will lead to high background signal and thus lower the sensitivity of the method.

Recently, excellent separation of transition metals have been obtained on a pellicular resin column using complexing agents as eluent (22). With low-capacity pellicular ion-exchange resin, the complexing agents offer the maximum separation of metal ions. In addition, a resin-based column does not have the pH limitations of a silica-based column and, therefore, is useful with eluents that are at pHs below 3.0. The pellicular resin column are thus being used more frequently in modern ion chromatography applications.

Current Knowledge on Ion Chromatography of Cr(III) and Cr(VI)

Determination of transition metals using liquid chromatographic methods has been simplified with the recent development of low cation-exchange capacity polymers. As shown by Sevenich and Fritz (11), selectivity and peak
sharpness can be enhanced by utilizing eluents containing complexing agents. Recent development efforts have produced new methods to determine a broad range of transition metals by using different complexing eluents and detectors \(24, 27\).

Because the cation suppression method precludes transition metal determinations, a post-column system has been developed, using post-column reaction of metals with PAR, followed by photometric detection. Very high sensitivities of detection (ppb) were possible. Although practical applications with PAR have previously been limited to several metals, recent reports have suggested the broader use of PAR for many additional transition metals \(28\). Currently, Cr(III) determination is being investigated by this method \(29\).

In addition to Cr(III) determination, oxidation state of Cr(VI) has been determined by using anion exchange chromatography \(3\). A similar detection of chromium by atomic absorption spectroscopy, only measures the total chromium present, including innocuous trivalent chromium, Cr(III), with no clue as to the ratios of the two species if present. This advantage make ion chromatography analysis of Cr(III) and Cr(VI) the perfect complement in laboratories employing only AA or ICP instrumentation.
Aquatic Chemistry of Chromium

Chromium is one of the d-block transition elements and has six valence electrons, $3d^54s^1$. Chromium occurs in valence states ranging from $-2$ to $+6$. Chromium (+6), which exists only as oxy species such as $\text{CrO}_3$, $\text{CrO}_4^{2-}$ and $\text{CrO}_2\text{F}_2$, is rather strongly oxidizing. Cr(+5) and (+4) are formed as transient intermediates in the reduction of Cr(+6) solutions; thus these oxidation states have no stable aqueous chemistry because of their ready disproportionation to Cr(+3) and Cr(+6). A fair number of Chromium (+2) compounds are known, all of which are strong and rapid reducing agents (30).

Chromium (+3) is the most stable and important oxidation state of the element in general and particularly in its aqueous chemistry. Trivalent chromium exhibits a strong tendency to form hexacoordinate octahedral complexes, with a great variety of ligands such as ammonia, urea, halides, sulfates, ethylenediamine, organic acids, proteins and peptides (31, 32). These complexes have great kinetic stability, but are thermodynamically unstable. Because of the kinetic inertness, many complex species can be isolated as solids and persist for relatively long periods of time in solution, even under conditions where they are thermodynamically quite unstable.

The chromium (+3) amines are perhaps the most numerous
and well-known complexes, for example,

\[ \text{[CrAm}_{6-n-m}\text{(H}_2\text{O})_n\text{R}_m\text{]}^{(3-m)+} \] (30). In the formula, Am represents the monodentate ligand NH$_3$ or half of a polydentate amine such as ethylenediamine, and R represents an acidic ligand such as a halide, nitro or sulfate ion. Also, in neutral and basic solutions, trivalent chromium forms polynuclear compounds in which adjacent chromium atoms are linked through \( \text{OH} \) or \( \text{O} \) bridges. These compounds may eventually precipitates as \( \text{Cr}_2\text{O}_3\cdot\text{nH}_2\text{O} \).

The hexaaqua ion \( \text{[Cr(OH}_2\text{)}_6\text{]}^{3+} \), which is octahedral, occurs in aqueous solution and in numerous salts such as \( \text{[Cr(H}_2\text{O})_6\text{]}\text{Cl}_3 \) (30). The aqua ion is acidic (pH 4), and the hydroxo ion condenses to give a dimeric hydroxo bridged species, \( \text{[(H}_2\text{O})_5\text{Cr(OH)}\text{Cr(H}_2\text{O})_5\text{]}^{4+} \).

Trivalent chromium reacts with aqueous hydroxide ion to form the insoluble chromic hydroxide, \( \text{Cr(OH)}_3\cdot\text{3H}_2\text{O} \). Spiccia and Marty (1986) (33) studied the chemical changes of chromium hydroxide, \( \text{Cr(OH)}_3\cdot\text{3H}_2\text{O} \). They found chromium hydroxide dissolves instantaneously in acid to form \( \text{Cr(OH}_2\text{)}_6^{3+} \). One minute after its precipitation in the pH range 8.5-9.7, acidification yields \( \geq 99.4\% \) of \( \text{Cr(OH}_2\text{)}_6^{3+} \) and \( \leq 0.6\% \) of hydrolytic oligomers \( \text{Cr}_n\text{(OH)}_r\text{O}_p\text{(aq)}^{(3n-r-2p)+} \) (n=2-4). Their results indicated when precipitates of chromium hydroxide are aged (\( t=10 \text{ min.-3 days} \)), the amount of \( \text{Cr(OH}_2\text{)}_6^{3+} \) recovered after rapid acid dissolution decrease with time and low (n=2-4) and higher (n>4) soluble
oligomers complete the material balance. They reported that these oligomers were kinetically stable and could be separated chromatographically.

Chromium (+6) is the highest oxidation state which forms oxo compounds, with the exception of CrF₆. Chromium (+6) does not give rise to an extensive and complex series of polyacids and anions characteristic of the less acidic oxides. This is probably due to the greater extent of multiple bonding of the smaller chromium ion. The main oxoacids or anions of hexavalent chromium are the chromate and dichromate. Both the chromate and dichromate ions are strong oxidizing agents, especially in acid solution. Because they are highly poisonous, hexavalent chromium compounds have greater economic importance as well as biological and environmental significance.

In solutions above pH 6, CrO₃ forms the tetrahedral yellow chromate ion CrO₄²⁻; between pH 2 and 6, the bichromate ions (HCrO₄⁻) and the orange-red dichromate ion (Cr₂O₇²⁻) are in equilibrium; and at pH values below 1 the main species is H₂CrO₄ (30). All of the anionic forms are quite soluble, and are thus quite mobile in the aquatic environment (34). The equilibria are the following (30):

\[
\begin{align*}
\text{HCrO}_4^- & \rightleftharpoons \text{CrO}_4^{2-} + \text{H}^+ & K = 10^{-5.9} \\
\text{H}_2\text{CrO}_4 & \rightleftharpoons \text{HCrO}_4^- + \text{H}^+ & K = 4.1 \\
\text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O} & \rightleftharpoons 2 \text{HCrO}_4^- & K = 10^{-2.2}
\end{align*}
\]
The pH-dependent equilibria are quite labile, and on addition of cations that form insoluble chromates (e.g., Ba\(^{2+}\), Pb\(^{2+}\), Ag\(^{+}\)) the chromates, and not the dichromates, are precipitated.

In acid solution, the dichromate ion is a powerful oxidizing agent:

\[
\text{Cr}_2\text{O}_7^{2-} + 14 \text{ H}^+ + 6 \text{ e}^- \rightleftharpoons 2 \text{ Cr}^{3+} + 7 \text{ H}_2\text{O} \quad \text{E}^0 = 1.33 \text{ V}
\]

In basic solution, however, the chromate ion is much less oxidizing:

\[
\text{CrO}_4^{2-} + 4 \text{ H}_2\text{O} + 3 \text{ e}^- \rightleftharpoons \text{Cr(OH)}_3^{(s)} + 5 \text{ OH}^- \quad \text{E}^0 = -0.13 \text{ V}
\]

Hexavalent chromium can be reduced in natural waters containing organic matter to Cr\(^{3+}\), which would be precipitated as the hydroxide. Schroeder and Lee (1975) (35) studied the transformation of chromium in natural waters. Their results have indicated that Cr\(^{+6}\) could be reduced by Fe\(^{+2}\), dissolved sulfides, and certain organic compounds with sulfhydryl groups, while Cr\(^{+3}\) could be oxidized by a large excess of MnO\(_2\) and at a slower rate by oxygen.

Thermodynamic properties and environmental chemistry of chromium, has been recently reviewed by Schmidt (36). These data were used to construct Eh-pH diagram Figure 2 (37) at total Cr concentration of \(1.92 \times 10^{-4} \text{ M}\).
Figure 2. Eh-pH diagram based on experimental waters Cr concentration.
(from reference 37)
Chapter Bibliography


CHAPTER II

EXPERIMENTAL

Instrumentation

The ion chromatograph consisted of a Waters Assoc. Model 501 solvent delivery system, containing a pump and electronics units, and a Model 430 conductivity detector. A single-channel recorder/integrator (Waters 740 data module) was used to record the chromatograms. Periodically, a Linear instrument dual-channel 1200 recorder was used. Figure 3 shows a schematic diagram of the ion chromatography instrument. The operating conditions are shown on Table I.

Atomic absorption measurements were carried out on a Perkin-Elmer 2380 atomic absorption spectrophotometer with a HGA 400 graphite furnace. The light source was chromium (Fisher Scientific Co.) hollow cathode lamp. Operating conditions are shown on Table II.

A Bausch & Lomb Spectronic 20 spectrophotometer was used for colorimetric measurement of Cr(VI)(1). Measurements were made in a 1.0 cm glass cell.
Figure 3. Schematic diagram of IC with conductivity detector.
Table I

ION CHROMATOGRAPHY PARAMETERS

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Separator Column</td>
<td>Waters IC-PAK Cation Column</td>
</tr>
<tr>
<td></td>
<td>Waters IC-PAK Anion Column</td>
</tr>
<tr>
<td>Guard Column</td>
<td>Waters Guard-PAK Precolumn</td>
</tr>
<tr>
<td>Flow Rate</td>
<td>1.0-1.2 ml/min.</td>
</tr>
<tr>
<td>Injection Volume</td>
<td>20-100 μl</td>
</tr>
<tr>
<td>Chart Speed</td>
<td>0.5 cm/min.</td>
</tr>
</tbody>
</table>
Table II

ATOMIC ABSORPTION SPECTROPHOTOMETER PARAMETERS

<table>
<thead>
<tr>
<th>Light Source</th>
<th>Cr Hollow Cathode Lamp</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelength</td>
<td>589.0 nm</td>
</tr>
<tr>
<td>Slit Width</td>
<td>0.7 nm</td>
</tr>
<tr>
<td>Flame</td>
<td>Air-Acetylene, Reducing</td>
</tr>
<tr>
<td></td>
<td>(Rich, Yellow)</td>
</tr>
<tr>
<td>Sensitivity</td>
<td>0.31 mg/l</td>
</tr>
<tr>
<td>Detection Limit</td>
<td>0.01 ppm</td>
</tr>
<tr>
<td>Optimum Range</td>
<td>0.2-1.0 ppm</td>
</tr>
</tbody>
</table>
Columns

Four separating columns were used, two for anion separation and two for cation separation. No suppressor columns was used for the detection. The anion separating columns were; a) Waters IC-PAK anion exchange column (4.6 mm(ID) x 5 cm), packed with polymer-based anion exchanger, and b) Vydc 301 TP anion exchange column (4.6 mm(ID) x 25 cm) packed with a silica-based anion exchanger. For cation separation, the two columns were; a) Waters IC-PAK cation exchange column (4.6 mm(ID) x 5 cm) packed with polymer-based cation exchanger, and b) Vydc 401 TP cation exchange column (4.6 mm(ID) x 25 cm) packed with a silica-based anion exchanger. With the anion columns, a guard column (Waters Guard-PAK precolumn) was used to remove unwanted particulate and chemical contamination from the mobile phase. It was inserted into the IC system immediately before the analytical column. Table III. summarizes the properties of all the columns.

Both anion and cation silica-based columns were packed by a stirred slurry, upward packing method (2). The silica was packed in 5 % suspension of iso-propanol at about 3000 psi. After packing, the columns were rinsed by pumping Milli-Q water through the columns. Additional silica was added to the top of the columns as necessary. Equilibrium was established by flowing eluent through the column for several hours.
### Table III

**PROPERTIES AND DIMENSIONS OF THE SEPARATOR COLUMNS**

<table>
<thead>
<tr>
<th></th>
<th>Anion</th>
<th>Cation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>IC-PAK A</td>
<td>Vydac 301 TP</td>
</tr>
<tr>
<td>Packing Material</td>
<td>Polymethacrylate gel</td>
<td>Silica</td>
</tr>
<tr>
<td>Functionality</td>
<td>Quaternary ammonium</td>
<td>Quaternary amine</td>
</tr>
<tr>
<td>Exchange Capacity (meq/ml)</td>
<td>30 ± 3</td>
<td>-</td>
</tr>
<tr>
<td>Particle Size (μm)</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Column Dimension</td>
<td>4.6 x 5</td>
<td>4.6 x 25</td>
</tr>
<tr>
<td>(ID(mm) x L(cm))</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Eluent pH Range</td>
<td>1 - 13</td>
<td>2 - 7</td>
</tr>
<tr>
<td>Maximum Pressure (psi)</td>
<td>1000</td>
<td>1000</td>
</tr>
<tr>
<td>Maximum Flow Rate (ml/min)</td>
<td>1.2</td>
<td>-</td>
</tr>
</tbody>
</table>
Reagents

Standard Chromium Solutions

Cr(III) standard solutions were prepared by using the appropriate amount of reagent grade of CrCl$_3$·6H$_2$O (CAS Reg. 10060-12-5) and diluting with Milli-Q water to provide 100, 50, 10, and 1 ppm. Cr(VI) standard solutions were prepared by the appropriate dilution of 1000 ppm prepared (from K$_2$Cr$_2$O$_7$) (CAS Reg. 7778-50-9) standard stock solution using Milli-Q water. In the case of using EDTA as eluent, Cr(III) standard solution was prepared by diluting with 1 mM EDTA.

Eluents

A number of different eluents were chosen for use in this study. The eluents are summarized in Table IV. The materials used to prepare these solutions were ACS reagent-grade. The Millipore purification system (Bedford, MA, USA) was used to prepare high purity water. Eluents were filtered through a 0.45 μm membrane filter, and then a vacuum was applied while stirring to remove dissolved gas. The pH of the eluents was adjusted with potassium hydroxide or acetic acid.

Diphenylcarbazide

A 200 mg of s-diphenylcarbazide was dissolved in 100 ml
Table IV

ELUENTS USED WITH ANION AND CATION COLUMNS

<table>
<thead>
<tr>
<th>Eluents Used with Cation Columns</th>
<th>pH</th>
<th>Conductivity (μS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) 2mM HNO₃</td>
<td>2.85</td>
<td>800</td>
</tr>
<tr>
<td>(2) 0.67 mM EDA</td>
<td>6.07</td>
<td>272</td>
</tr>
<tr>
<td>(3) 5mM Oxalic acid</td>
<td>4.37</td>
<td>1350</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr(III)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(4) 5mM Oxalic acid</td>
<td>2.93</td>
<td>786</td>
</tr>
<tr>
<td>(5) 2mM LiH phthalate</td>
<td>3.5</td>
<td>171</td>
</tr>
<tr>
<td>(6) 10mM Tartaric acid</td>
<td>2.9</td>
<td>820</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Eluent Used with Anion Column</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(7) 1mM EDTA</td>
<td>4.0 - 5.5</td>
<td>240 - 276</td>
</tr>
</tbody>
</table>

Eluents Used with Anion Columns

| (1) 0.73 mM sodium gluconate       | 7.36 | 262               |
| 2.91 mM boric acid                 |      |                   |
| 0.66 mM sodium tetraborate         |      |                   |
| · 10H₂O                            |      |                   |
| 34.2 mM glycerin                   |      |                   |
| 2.3 M acetonitrile                 |      |                   |
| (2) 1.46 mM sodium gluconate       | 8.7  | 300               |
| 5.82 mM boric acid                 |      |                   |
| 1.32 mM sodium tetraborate         |      |                   |
| · 10H₂O                            |      |                   |
| 34.2 mM glycerin                   |      |                   |
| 2.3 M acetonitrile                 |      |                   |

Cr(VI)

| (3) 2.2 mM sodium gluconate         | 9.23 | 690               |
| 8.73 mM boric acid                 |      |                   |
| 1.98 mM sodium tetraborate         |      |                   |
| · 10H₂O                            |      |                   |
| 34.2 mM glycerin                   |      |                   |
| 2.3 M acetonitrile                 |      |                   |
of 95% ethanol, then 120 ml of 85% H₃PO₄ was added in 280 ml of distilled H₂O. A small amount of KMnO₄ was added until a pink color developed; then the mixture was heated to 60 °C until the color disappeared. The reagent kept 3 months with refrigeration (1).

Sources of Samples

Experimental water samples were prepared and collected in several different ways:

1. Synthetic EPA hard water: prepared according to Standard Methods of Examination of Water and Wastewater (3).
2. Cross Lake water: collected from the Cross Lake Reservoir, Shreveport, Louisiana.
3. Milli-Q water spiked with 10 mg/l ultra pure aquatic fulvic acid.

Procedure

A number of different eluents and two different columns (silica and polymer) were investigated for use in the Cr(III) determination by ion chromatography. The appropriate eluents, columns, and analytical conditions were selected for Cr(III) determination. Figures 4, 5, and 6 show the Cr(III) and Cr(VI) peaks in different eluents and systems.
Column: IC-PAK cation column
Mobile phase:
  10 mM Tartaric acid
  3.5 mM EDA
  5 % CH$_3$CN (pH 2.9)
Range: 1000 µS
Gain: 0.02

Figure 4. IC trace of Cr(III) determination; 5 ppm; injection volume, 100 µl; flow rate, 1.2 ml/min.
Figure 5. IC trace of Cr(III) determination; 5 ppm; injection volume, 100 ul; flow rate, 1.0 ml/min.
Column: IC-PAK anion column
Mobile phase:
- 2.2 mM sodium gluconate
- 8.73 mM boric acid
- 1.98 mM sodium tetraborate·10H₂O
- 34.2 mM glycerin
- 2.3x10⁻³ mM acetonitrile (pH 9.3)
Range: 1000 uS
Gain: 0.02

Figure 6. IC trace of Cr(VI) determination; 20 ppm; injection volume, 100 ul; flow rate, 1.2 ml/min.
For comparison of the IC technique, with the atomic absorption and colorimetric methods, a special study was conducted on the experimental waters. The following is a summary of the procedures for Cr(VI) and total Cr analysis:

Cr(VI) Determination

Hexavalent chromium was determined by the colorimetric diphenylcarbazide method as modified by Bartlett and James (1976) (1) using a Bausch and Lomb Spectronic 20. Aliquots (25 ml) of water samples were acidified with 6 N HCl to pH 1, then boiled for 30 min. The volume of the acidified residues were adjusted to 25 ml, then filtered through a 0.45 μm membrane filter. Ten milliliter of standard or sample was mixed with 0.5 ml of the carbazide reagent. Absorption was read after 10 min at 540 nm. The detection limit for the Cr(VI) was 0.02 mg/l.

Total Cr Determination

Total chromium was measured by the permanganate-azide methods outlined by APHA (1985) (4) using an atomic absorption spectrophotometer. Water samples were acidified by using the above procedure. After filtering with 0.45 μm membrane filter, both filter papers and appropriate amounts of solutions were digested with conc. HNO₃, KMnO₄, and quenched with NaN₃. The volume of the digested residues were adjusted to the same volume of the original samples.
Chapter Bibliography


CHAPTER III

RESULTS AND DISCUSSIONS

This chapter includes the following sections:

- Cr(III) Determination by Cation Exchange Column
- Cr(III) Determination by Anion Exchange Column
- Cr(VI) Determination by Anion Exchange Column
- Silica Based Cation and Anion Exchange Columns

Cr(III) Determination by Cation Exchange Column

As discussed in the literature review, the eluent must be carefully chosen when a conductivity detector is used. Generally, transition metal ions are too strongly retained to be eluted by monovalent driving ion such as the hydronium. A complexing agent is normally required in order to reduce the metals charge density. Typical complexing agents are citric acid, oxalic acid, tartaric acid, and ethylenediamine. Eluents containing the ethylenediammonium cation and either tartrate or hydroxyisobutyrate as the complexing anion have been successfully used for Mn$^{2+}$, Co$^{2+}$, Zn$^{2+}$, Cd$^{2+}$, and Pb$^{2+}$ as well as the lanthanides (1, 2).

In the separation of polyvalent metal ions, eluent pH and concentration may have a dramatic effect on the
resolution and retention. For Cr(III) ions, the situation is further complicated due to the formation of the different hydrated species with charges ranging from +3 to -1.

Six eluents (Table IV) were evaluated for Cr(III) determination with the cation column. The first eluent consisted of 2 mM HNO₃ and was recommended by the manufacturer, but did not give satisfactory results. Eluents number 2-5 satisfied the essential criteria of eluents in polyvalent cations separation. However no satisfactory results were obtained with Cr(III). With the cation column the best results were obtained with eluent No. 6. As shown in Figure 4 the retention time of Cr(III) standard solution was 4.4 minutes under the flow of 1.2 ml/min which corresponds to k' of 10.61. The plot of peak area vs. the concentration of Cr(III) gives a linear relationship over the range of 0.5-10.0 ppm, with a correlation coefficient 0.998 (Figure 7). The detection limit of Cr(III) with this eluent is 0.1 ppm, based on 100 μl sample injection.

Eluent No. 6, contains the ethylenediammonium as the exchange cation and the tartrate ligand as the complexing agent. At pH 2.9 the dissociation of tartaric acid is limited (Table V) and Cr(III) is likely to form a soluble chelate with the tartaric acid ligand. It appears that the elution mechanism involves a combination of the mass action "pushing" effect of the ethylenediammonium cation and the
Figure 7. Calibration curve for Cr(III) determination; 0.5-10.0 mg/L; injection volume, 100 ul.
Table V

FRACTIONS OF TARTARIC ACID \(^a\) AT PH 2.9

<table>
<thead>
<tr>
<th>(\alpha) (^b)</th>
<th>pH 2.9</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\alpha_0)</td>
<td>5.38 \times 10^{-1}</td>
</tr>
<tr>
<td>(\alpha_1)</td>
<td>4.44 \times 10^{-1}</td>
</tr>
<tr>
<td>(\alpha_2)</td>
<td>1.60 \times 10^{-2}</td>
</tr>
</tbody>
</table>

\(^a\) \(K_1 = 1.04 \times 10^{-3}\)
\(K_2 = 4.55 \times 10^{-5}\)

\(^b\)  

\[
\alpha_0 = \frac{[H_2Y]}{C_T} = \frac{[H^+]^2}{[H^+]^2 + K_1[H^+] + K_1K_2}
\]

\[
\alpha_1 = \frac{[HY^-]}{C_T} = \frac{K_1[H^+]}{[H^+]^2 + K_1[H^+] + K_1K_2}
\]

\[
\alpha_2 = \frac{[Y^{2-}]}{C_T} = \frac{K_1K_2}{[H^+]^2 + K_1[H^+] + K_1K_2}
\]
weakly complexing or "pulling" effect of the tartrate anion (1). The amine is double protonated at low pH and hence is very effective as a counter ion in the mobile phase, but contributes insignificantly to the complexation of Cr(III). The eluted metal ions are only partly complexed and are mostly in solution as cations. The eluted ions have a lower equivalent conductance than the eluent cation and thus appear as peaks of lower conductance.

The mechanism of elution using ethylenediammonium and the tartrate can be explained as follows:

\[ 2 \text{M}^+ \text{R}_y + y \text{E}^{2+} \rightleftharpoons y \text{E}^{2+} \text{R}_2 + 2 \text{M}^+ \] (3.1)

where \( \text{E}^{2+} \) represents the eluent cation (ethylenediammonium), \( \text{M}^+ \) represents the sample metal ion, and the subscript on \( \text{R} \) represents the exchange sites on the resin used by the ion. The selectivity coefficient, \( K_{\text{M}}^E \), for this reaction is:

\[ K_{\text{M}}^E = \frac{[\text{E}^{2+}\text{R}_2]^y [\text{M}^+]^2}{[\text{E}^{2+}]^y [\text{M}^+\text{R}_y]^2} \] (3.2)

At low loading of sample ion, the resin capacity/2 is approximately \( [\text{E}^{2+}\text{R}_2] \). The capacity factor, \( k' \), is equal to the ratio \( [\text{M}^+\text{R}_y]/ [\text{M}^+] \). Thus the equation can be written as:
The adjusted retention time, $t$, for an eluted peak is equal to $t_0k'$, where $t_0$ is the retention time of an unretained substance. Substituting $t/t_0$ for $k'$ and taking logarithms gives:

$$\log t = \frac{Y}{2} \log \left(\frac{\text{Cap}}{2}\right) + \log t_0 - \frac{Y}{2} \log [E^{2+}] - \frac{1}{2} \log K_M^E$$

(3.4)

In eluents containing a complexing anion such as tartrate, some of the metal cations will be in solution as a neutral or anionic complex. The effect of this complexing on the exchange equilibrium can be calculated by methods worked out primarily by Ringbom (3). Substituting $[M']\alpha_M$ for $[M'^+]$ in eqn 3.2, where $[M']$ is the sum of free and complexed metal in solution and $\alpha_M$ is the fraction of the metal in solution that exists as the free cation. The capacity factor, $k'$, is now the ratio of $[M'^+R_y]$ to $[M']$. Continuing the derivation as before, the new equation can be written as:
\[
\log t = \frac{Y}{2} \log \alpha_M + \frac{Y}{2} \log \left(\frac{\text{Cap}}{2}\right) + \log t_0
\]

\[
- \frac{Y}{2} \log [E^{2+}] - \frac{1}{2} \log K_M^e
\]  

(3.5)

The validity of eqn. 3.4 can be evaluated by measuring the adjusted retention times of a number of cations at constant concentration of tartrate and pH but at varying concentrations of ethylenediammonium cation in the eluent. A plot of the logarithm of the adjusted retention times vs. the logarithm of the concentrations of ethylenediammonium cation would produce a straight line. The theoretical slope of the linear line would be -1.5 for a +3 cations and -1.0 for a +2 cations. Sevenich and Fritz (1) applied this method to the separation of rare earth ions and divalent metal ions. The slope was -1.0 for rare earth ions and -0.9 for divalent cations.

Linear plots can also be obtained from eqn. 3.5 when the concentration of tartrate in the eluent was varied and the log of adjusted retention time is plotted against log \(\alpha_M\). It has been shown that the retention time decreased as more tartrate was used in the eluent (1).

Using eluent No. 6, the retention time and peak symmetry seemed satisfactory for practical application. It was then decided to use this method on a regular bases for analysis of soluble Cr(III). With the continued use of the
procedure, some operational problems were incurred. The following summarizes these problems and the recommended methods to alleviate them:

The Stability of the Cr(III) Standard Solution

It was noted that the storage time of the standard solution has a direct effect on the reproducibility and the linearity of Cr(III) determination. When Cr(III) standard solution was stored more than 24 hours, the slope of the calibration curve has declined relative to the case when a fresh Cr(III) standard solution was used. Figure 8 shows the decline of the slope of the calibration curve with aging of the standard solution. This occurs most often when Cr(III) reacts with aqueous hydroxide ion to form the insoluble chromic hydroxide, Cr(OH)$_3$. Usually Cr(III) precipitates to Cr(OH)$_3$·nH$_2$O in neutral or basic solution. The recommendation with respect to Cr(III) standard solution is to control the pH range of Cr(III) standard solution in acidic condition to prevent the precipitation of Cr(OH)$_3$, which begins at ca. pH 4-5, and to use fresh standard solution which is prepared every day.

Cr(III) Recovery

After extended use of the cation column (ca. two months), IC peak splitting started to appear. The tailing of the Cr(III) peak could be due to the IC column
Figure 8. Declination of Cr(III) calibration curve with aging of Cr(III) standard solution, mobile phase: 10 mM tartaric acid, 3.5 mM EDA, and 5 % CH$_3$CN.
degradation or due to the formation of a new Cr(III) ion exchange species. This is quite possible in view of the formation of several Cr(III) hydrated oligomers upon aging of Cr(OH)$_3$·nH$_2$O (4).

An experiment was conducted to evaluate Cr(III) recovery from the unretained volume and the two split peaks in Figure 9. Ten 100 µl injections of 4 ppm CrCl$_3$·6H$_2$O standard solution were introduced to IC and three fractions representing, the unretained volume, peak 1, and peak 2, were collected and oxidized using the permanganate-azide method (5), and the volume of the samples were optimally adjusted to the AA detection range.

Results are shown in Table VI. The error in the mass balance is only 0.75 %. The solvent peak contained 11.4 % of the eluted Cr(III), and peak 1 and 2 contained 74.4 % and 14.1 % of the Cr(III), respectively. These results indicate that Cr(III) was present in all of the three peaks, and that 88.5 % of the Cr(III) are retained by the ion exchange mechanism. The results also indicate that 11.4 % of the Cr(III) are not retained by the column indicating no interaction with the column or fast ion exchange mechanism. The portion of Cr(III) in the tailing peak is probably due to the decrease of column efficiency or the presence of different species of chromium in sample solution. Further studies are needed on this part.
Figure 9. IC trace of Cr(III) fractions recovery.
Table VI

**QUANTITATIVE ANALYSIS OF Cr(III) FRACTIONS RECOVERY**

<table>
<thead>
<tr>
<th>Peak</th>
<th>Mass (mg)</th>
<th>Recovery of Cr (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solvent Peak</td>
<td>$4.6 \times 10^{-4}$</td>
<td>11.4</td>
</tr>
<tr>
<td>Peak 1</td>
<td>$3.0 \times 10^{-3}$</td>
<td>74.4</td>
</tr>
<tr>
<td>Peak 2</td>
<td>$5.7 \times 10^{-4}$</td>
<td>14.1</td>
</tr>
</tbody>
</table>

Total Mass

\[
M_{\text{Exp}} = 4.03 \times 10^{-3}
\]

\[
M_{\text{Cal}} = 4.00 \times 10^{-3}
\]

Error (%): + 0.75

*Column: IC-PAk cation column

Mobile phase: 10 mM Tartaric acid
3.5 mM EDA
5 % CH$_3$CN

Flow rate: 1.2 ml/min
Column Regeneration

With repeated injections of standard and samples, the column efficiency decreased. This resulted in: loss of resolution, peaks broadening and tailing, and decrease of retention time. Residual polyvalent cations of Cr(III) would be strongly held by the resins and would not be eluted by the eluent used in this research. As a result, the number of available exchange sites on the resin decreased causing a degradation of the column. These strongly held cations were removed from the column by slowly purging (below 1 ml/min) 50 ml of 100 mM HNO₃. This solution assist in the rapid elution of the polyvalent cations and allow for use of the column after re-equilibration with the mobile phase.

Applications

The IC procedure using the cation column and eluent No. 6 were applied to three experimental water samples which have been spiked with 24-hour-aged Cr(OH)₃.

The Cr(III) hydroxide were prepared by dissolving 0.2050 g of reagent grade of CrCl₃·6H₂O in 30 ml Milli-Q water and precipitating the hydroxides by adding 6 N NaOH solution to pH 12. The total volume was adjusted to 250 ml and the pH was adjusted to pH 7. This slurry was used as a source of Cr(III) after aging for 24 hours. Then, the three
experimental waters were spiked with 24-hour-aged Cr(OH)$_3$ at a concentration of 10 mg/l. Sample bottles were kept on a shaker table with gentle shaking action.

At sampling time, a 25 ml sample was subjected to the outline in Figure 10. Aliquots (10 ml) of water samples were acidified and filtered then freeze dried by a Labconco Freeze Dryer. The freeze-dried residues were solubilized in mobile phase (10 mM Tartaric acid, 3.5 mM EDA, and 5% CH$_3$CN, pH 2.9) and adjusted to the same volume of the original samples. This method was developed to avoid the big negative peak due to HCl. Cr(III) was determined by injection of the samples into a cation column and elution with ethylenediammonium tartrate solution. To compare the IC results, soluble Cr(III) sample solutions left from IC analysis were digested with KMnO$_4$ and HNO$_3$ and tested by AA and Spect. 20 for determination of total Cr and Cr(VI).

The results are shown in Table VII. The table shows that the average recovery of Cr from HCl treatment is 91.6 percent. Thus 6 N HCl and heating are adequate steps to solubilize Cr(OH)$_3$·nH$_2$O in suspension. Table VII also shows good agreement between the IC method and the AA method, after solubilization with HCl. Furthermore no Cr(VI) was detected by the spectrophotometric method. These results were obtained only with freshly spiked samples. As the samples aged, the IC procedures gave lower recoveries.
Figure 10. Outline of the sample preparation and analysis methods for experimental water samples.

- 25 ml 10 ppm Cr(OH)₃
- add 6 M HCl to pH 1
- boil 30 min until clear
- volume adjusted to 25 ml
- filtered
- filter paper (insoluble Cr)
- filter paper placed in vial with 10 ml MQ water
- digested with KMnO₄, HNO₃ and quenched with NaN₃
- volume adjusted to 25 ml
- 10 ml of sample freeze dry
- 10 ml of sample dilute to 2-2 ml aliquots
- solution (soluble Cr)
- 10 ml of sample add 0.5 ml of DPC
- Spect-20 analysis at 540 nm
- IC analysis
- volume adjusted to 25 ml
- *Mobile phase:
  - 10 mM Tartaric acid
  - 3.5 mM EDA
  - 5% CH₃CN (pH 2.9)

AA analysis
<table>
<thead>
<tr>
<th></th>
<th>Hard Water (pH 7.9)</th>
<th>Cross Lake Water (pH 7.2)</th>
<th>Milli-Q Water &amp; Fulvic Acid (pH 4.5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial Total Cr (mg/L) AA</td>
<td>8.88</td>
<td>8.94</td>
<td>9.25</td>
</tr>
<tr>
<td>HCl Soluble Cr (mg/L) AA</td>
<td>8.44</td>
<td>8.19</td>
<td>7.56</td>
</tr>
<tr>
<td>Percent Soluble Cr (%)</td>
<td>96.06</td>
<td>92.23</td>
<td>81.08</td>
</tr>
<tr>
<td>HCl Insoluble Cr (mg/L) AA</td>
<td>ND*</td>
<td>ND</td>
<td>0.5</td>
</tr>
<tr>
<td>Total Recovery of Cr from HCl Treatment (%)</td>
<td>96.06</td>
<td>92.23</td>
<td>86.49</td>
</tr>
<tr>
<td>Total Cr(III) from IC (mg/L)</td>
<td>8.64</td>
<td>7.82</td>
<td>8.18</td>
</tr>
<tr>
<td>Recovery of Soluble Cr by IC (mg/L)</td>
<td>101.29</td>
<td>94.79</td>
<td>109.07</td>
</tr>
<tr>
<td>HCl Soluble Cr(VI) by Spect.20 (mg/L)</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
</tr>
</tbody>
</table>

*ND: Not detected

Recovery of Soluble Cr by IC (%) = Total Cr(III) from IC/HCl Soluble Cr x 100%
Cr(III) Determination by Anion Exchange Column

Eluent No. 7 consisted of 1 mM EDTA was used at the pH range 4.0-5.5 for Cr(III) determination with the anion exchange column. EDTA is a strong chelating agent, which form complexes with Cr(III). The anionic Cr-EDTA complex can be easily eluted from the column due to its reduced charge density.

In recent work, ethylenediaminetetraacetate (EDTA) has been used to separate transition metals such as Zn$^{2+}$, Mn$^{2+}$, Cu$^{2+}$, Fe$^{2+}$, and Ni$^{2+}$ (6). Because EDTA has a -4 charge, it is expected to have a high affinity for the anion exchanger and to be an effective eluting agent and also has lower equivalent conductance than inorganic anions.

The dissociation constants of EDTA, $H_4Y$, at 20 °C and an ionic strength of 0.1, are $pK_1 = 2.0$, $pK_2 = 2.67$, $pK_3 = 6.16$, and $pK_4 = 10.26$ (7). The distribution of the acidic protons are a function of the degree of ionization. The fraction of EDTA existing as $H_4Y$, $H_3Y^-$, $H_2Y^{2-}$, $HY^{3-}$, and $Y^{4-}$ can be calculated at various pH values by the following equations:

$$\alpha_0 = \frac{[H_4Y]}{C_T} = \frac{[H^+]^4}{[H^+]^4 + K_1[H^+]^3 + K_1K_2[H^+]^2 + K_1K_2K_3[H^+] + K_1K_2K_3K_4}$$

$$\alpha_1 = \frac{[H_3Y^-]}{C_T} = \frac{K_1[H^+]^3}{[H^+]^4 + K_1[H^+]^3 + K_1K_2[H^+]^2 + K_1K_2K_3[H^+] + K_1K_2K_3K_4}$$
\[
\alpha_2 = \frac{[H_2Y^{2-}]}{C_T} = \frac{K_1K_2[H^+]^2}{[H^+]^4 + K_1[H^+]^3 + K_1K_2[H^+]^2 + K_1K_2K_3[H^+] + K_1K_2K_3K_4}
\]
\[
\alpha_3 = \frac{[HY^{3-}]}{C_T} = \frac{K_1K_2K_3[H^+]}{[H^+]^4 + K_1[H^+]^3 + K_1K_2[H^+]^2 + K_1K_2K_3[H^+] + K_1K_2K_3K_4}
\]
\[
\alpha_4 = \frac{[Y^{4-}]}{C_T} = \frac{K_1K_2K_3K_4}{[H^+]^4 + K_1[H^+]^3 + K_1K_2[H^+]^2 + K_1K_2K_3[H^+] + K_1K_2K_3K_4}
\]

where \( K_1, K_2, \ldots \) are stepwise dissociation constants, and \( C_T \) is the total concentration of each fraction. Values for \( \alpha_0, \alpha_1, \alpha_2, \alpha_3 \) and \( \alpha_4 \) at various pH values are given in Table VIII.

For metal ions, the major species present in the formation of metal-EDTA complexes may be represented by the equations:

\[
M^{2+} + H_2EDTA^{2-} \rightleftharpoons MEDTA^{2-} + 2 H^+ \quad \text{pH} 4 \text{ to } 5;
\]
\[
M^{3+} + H_2EDTA^{2-} \rightleftharpoons MEDTA^- + 2 H^+ \]
\[
M^{2+} + HEDTA^{3-} \rightleftharpoons MEDTA^{2-} + H^+ \quad \text{pH} 7 \text{ to } 9;
\]
\[
M^{3+} + HEDTA^{3-} \rightleftharpoons MEDTA^- + H^+
\]

The elution behavior with EDTA as eluent can be analyzed as follows. The anion-exchange equilibrium is represented by:

\[
x S_y^- R_y + y E^{x-} \rightleftharpoons y E^{x-} R_x + x S_y^- \quad (3.6)
\]

where \( S_y^- \) represents the sample anion and \( R_x, R_y \) the exchange sites on the resin used by the ions, and \( E^{x-} \) the
Table VIII

FRACTIONS OF EDTA AS $H_4Y$, $H_3Y^-$, $H_2Y^{2-}$, $HY^-$, AND $Y^-$

<table>
<thead>
<tr>
<th>$\alpha$</th>
<th>$\alpha_0$</th>
<th>$\alpha_1$</th>
<th>$\alpha_2$</th>
<th>$\alpha_3$</th>
<th>$\alpha_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>3.0</td>
<td>4.0</td>
<td>4.5</td>
<td>5.0</td>
<td>5.5</td>
</tr>
<tr>
<td></td>
<td>$3.03 \times 10^{-2}$</td>
<td>$4.35 \times 10^{-4}$</td>
<td>$4.41 \times 10^{-5}$</td>
<td>$4.27 \times 10^{-6}$</td>
<td>$3.75 \times 10^{-7}$</td>
</tr>
<tr>
<td></td>
<td>$3.09 \times 10^{-1}$</td>
<td>$4.43 \times 10^{-2}$</td>
<td>$1.43 \times 10^{-2}$</td>
<td>$4.36 \times 10^{-3}$</td>
<td>$1.21 \times 10^{-3}$</td>
</tr>
<tr>
<td></td>
<td>$6.61 \times 10^{-1}$</td>
<td>$9.48 \times 10^{-1}$</td>
<td>$9.65 \times 10^{-1}$</td>
<td>$9.32 \times 10^{-1}$</td>
<td>$8.20 \times 10^{-1}$</td>
</tr>
<tr>
<td></td>
<td>$4.58 \times 10^{-4}$</td>
<td>$6.57 \times 10^{-3}$</td>
<td>$2.11 \times 10^{-2}$</td>
<td>$6.45 \times 10^{-2}$</td>
<td>$1.79 \times 10^{-1}$</td>
</tr>
<tr>
<td></td>
<td>$2.52 \times 10^{-11}$</td>
<td>$4.00 \times 10^{-9}$</td>
<td>$3.68 \times 10^{-8}$</td>
<td>$3.55 \times 10^{-7}$</td>
<td>$3.12 \times 10^{-6}$</td>
</tr>
</tbody>
</table>
eluent anion (EDTA).

The selectivity coefficient, $K_M^E$, for this reaction is:

$$K_M^E = \frac{[E^{x-R}] [S^{y-}]^x}{[E^{x-}] [S^{y-R}]^x}$$  \hspace{1cm} (3.7)

Continuing the derivation as mentioned before, equation 3.7 can be written as:

$$\log t = \frac{Y}{x} \log (\text{Cap}) - \frac{Y}{x} \log [E^{x-}] + \log t_0 - \frac{1}{x} \log K_M^E$$  \hspace{1cm} (3.8)

For trivalent metal complex anions equation 3.6 can be written as:

$$3 \text{MEDTA}^- R + \text{HEDTA}^3^- \rightleftharpoons \text{HEDTA}^{3-R}_3 + 3 \text{MEDTA}^-$$  \hspace{1cm} (3.9)

Table IX shows the retention times and capacity factors of CrEDTA$, Cl^-, NO_3^-$, and SO$_4^{2-}$. All of these ions were eluted within 16 min. The calibration curve of Cr(III) by peak height is showed in Figure 11.

Control of eluent pH can be very useful in adjusting the retention time of metal ions. Figure 12 shows the effect of pH on the retention time of the ions. The retention times decreased with increasing the pH from 4.0-5.5. This is due to the increase in concentration of HEDTA$^{3-}$. Partitioning of the metal ion in the eluent increases due to the enhanced complexation. This shifts the
<table>
<thead>
<tr>
<th>Ions</th>
<th>R.T. (min.)</th>
<th>$k'$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CrEDTA$^-$</td>
<td>2.5</td>
<td>1.5</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>4.4</td>
<td>3.4</td>
</tr>
<tr>
<td>NO$_3^-$</td>
<td>12.4</td>
<td>11.4</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>15.4</td>
<td>14.4</td>
</tr>
</tbody>
</table>

*mobile phase: 1mM EDTA

flow rate: 1.0 ml/min
Figure 11. Calibration curve for Cr(III) determination; 1.0-10.0 mg/L; injection volume, 100 ul.
Figure 12. Variation of Cr(III) retention with change of pH 4.0-5.5; Cr(III) concentration, 5 ppm; injection volume, 100ul; eluent, 1 mM EDTA; flow rate, 1.0 ml/min.
equilibrium of the metal ion from the resin to the complexing eluent, thus, decreasing retention.

Figure 12 shows a large negative chloride peak partially overlapped with the small chromium peak at some pH values. Comparison of the responses and separations in different pH values of eluent can be seen in this figure. The results indicate that pH 5.0 is a more suitable pH value than others.

The detector response of a sample depends on the relative equivalent conductances of the sample and eluent ions. The sample ions must have a lower equivalent conductance than the eluent anion to give a positive peak. In this case, Cr-EDTA complex has lower equivalent conductance than EDTA eluent, which appears as a positive peak. Inorganic anions such as Cl- give a negative peak because they have higher equivalent conductance than the EDTA eluent.

From Figure 11, a calibration plot of peak height vs. chromium ion concentration is very linear (with the correlation coefficient equal to 0.995) in the range of 1.0-10.0 ppm. Because the chromium ion peak partially overlapped with the chloride ion peak, quantitative measurement by using peak heights is better than peak areas. The detection limit can be defined as the concentration of the sample of interest when peak height or peak area is greater than twice the base-line noise. For chromium ion
with 1 mM EDTA eluent, the detection limit is 0.5 ppm based on 100 μl sample injection.

In this case, although conductometric detection is satisfactory in terms of speed and simplicity, the detection limit for Cr(III) is quite high. This is because the difference between the relative equivalent conductance of Cr-EDTA complex and the EDTA eluent is small. The complexing agent, EDTA, has weak absorbance in the 210-240 nm region; thus the UV detector can be applied and hence better detection limits can be achieved.

Cr(VI) Determination by Anion Exchange Column

The main objective of this research was to develop an ion chromatography methodology for Cr(III) determination, a secondary objective was to evaluate the determination of Cr(VI) with anion exchange chromatography. In this study potassium dichromate, K$_2$Cr$_2$O$_7$, was used for Cr(VI) standard sample. First, lower concentration of borate buffer solution was selected as eluent, but Cr$_2$O$_7^{2-}$ sample was eluted very late at about 28 min, and sample peak was very broad. By increasing concentration of eluent, retention time of Cr$_2$O$_7^{2-}$ became shorter. It was found that the most appropriate eluent for Cr(VI) determination was eluent No. 3 in Table IV. This eluent gave retention time of approximately 11 min for Cr$_2$O$_7^{2-}$ sample. Figure 6 shows the
chromatogram of Cr$_2$O$_7^{2-}$ analysis by IC with a conductivity detector.

The plot of peak area vs. the concentration of Cr(VI) gave a linear relationship over the range of 1.0-10.0 ppm and 10.0-100.0 ppm with a 20 μl injection loop (Figure 13, 14). The correlation coefficients for the ranges (1.0-10.0 ppm and 10.0-100.0 ppm) were 0.993 and 0.998, respectively. The detection limit of a Cr(VI) sample is 0.5 ppm with a 20 μl injection loop. The detection limit can be improved by using a larger sample injection loop.

Silica Based Cation and Anion Exchange Columns

Silica based ion exchange packings are reported to give better separation efficiency, especially for transition metals. However it can not be used below pH 3 or above pH 7.

In this research, two Vydac silica-based columns (cation and anion) were packed by a stirred slurry, upward packing method (7). The two columns were used for determination of Cr(III) and Cr(VI). Both of two columns revealed poor resolution, perhaps due to the insufficient packing equipment and technique.
Figure 13. Calibration curve for Cr(VI) determination; 1.0-10.0 mg/L; injection volume 20 ul.
Figure 14. Calibration curve for Cr(VI) determination; 10-100 mg/L; injection volume, 20 ul.
Chapter Bibliography


CHAPTER IV

CONCLUSION

Ion chromatographic methods for analysis of Cr(III) and Cr(VI), in aqueous samples were investigated. An IC methodology for Cr(III) was developed and evaluated for a period of one year. The method involves the use of cation column with an eluent containing tartaric acid, ethylenediamine, and acetonitrile at pH 2.9; and a conductivity detector. The detection limit of this method can reach 0.1 ppm level with good precision. Several operational parameters were evaluated during the regular use of the method.

It was observed that when Cr(III) standard solution was stored more than 24 hrs, the slope of the calibration curve declined relative to the fresh standard solution. The recommendation for the standard solution is to keep the pH in acidic condition and to use fresh standard solution which is prepared every day. In the Cr(III) recovery study, it was shown that only 88.5 % of Cr(III) sample was retained on the column and for 4-6 minutes. The IC method of Cr(III) was applied to three experimental water samples spiked with Cr(OH)₃. A freeze-dried method was used for sample pretreatment. Comparison of the IC method with AA method,
showed good agreement between the two methods. A column regeneration method was used in this research to elute the accumulated polyvalent cations which were strongly held in the column.

The anion column was also used for Cr(III) determination by using an eluent which consisted of 1 mM EDTA. A linear relationship in the range of 1.0-10.0 ppm was obtained; however, further studies would be necessary to improve the detection limit. The study of the effect of pH on retention revealed the retention times decreased with increasing pH from 4.0-5.5.

Cr(VI) determination by anion exchange column was evaluated. The best results were obtained with eluent containing sodium gluconate, boric acid, sodium tetraborate, glycerin, and acetonitrile (eluent No. 3 in Table IV). The retention time for Cr$_2$O$_7^{2-}$ sample was 11 min. and the calibration curve was linear between 1.0 and 100 ppm.

In summary, separation by ion chromatography followed by conductivity detection is a quick and simple method for the determination of Cr(III) and Cr(VI). The use of these methods allows the routine analysis of Cr(III) and Cr(VI) by IC.
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