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ABSTRACT

DEVELOPMENT OF METHODS FOR FIELD DETERMINATION OF CHROMIUM (VI) IN WATER AND GROUNDWATER

by David John Chesbro

In this study, methods for the determination of chromium (VI) in fresh water at low ppb levels for the use under field conditions were developed. The plan was to devise a simple and inexpensive on-site field method which would be useable by people who are not professional chemists. An investigation was carried out to develop a preconcentration and determination procedure for the analysis of chromium (VI) using anion-exchange membranes and/or resins. The chromium (VI) would be sorbed to the solid support and then treated with 1,5-diphenylcarabzide, a specific colorimetric reagent for chromium (VI), which forms a red complex upon reaction. A simple preconcentration procedure, and a portable colorimeter were used to make the method suitable for field use. Sensitivity, selectivity and precision are evaluated to ensure that the method to provides accurate and reliable results in the field.

DEVELOPMENT OF METHODS FOR FIELD DETERMINATION OF CHROMIUM (VI) IN WATER AND GROUNDWATER

by David John Chesbro

A Thesis Submitted to the Faculty of New Jersey Institute of Technology in Partial Fulfillment of the Requirements for the Degree of Masters of Science

> Department of Chemical Engineering, Chemistry, and Environmental Science

> > May 1997

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APPROVAL PAGE

DEVELOPMENT OF METHODS FOR FIELD DETERMINATION OF CHROMIUM (VI) IN WATER AND GROUNDWATER

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To my beloved Family and Friends

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CHAPTER 1

INTRODUCTION

In recent years, the use of on-site methods for analysis of environmental samples has become more prevalent in the environmental field. Over the past four years, companies manufacturing field test equipment grew an average of 15% per year, while the rate of growth in the fixed laboratory industry has slowed down dramatically, from a high of 15% to a current rate of 2-4%.¹ The major reason for this change in methodology occurred because it had been determined that approximately eighty percent of the errors in off-site analysis could be attributed to the transportation and mishandling of samples.² It has been estimated that the cost of transporting samples can add between forty and eighty dollars to the total cost per sample.³ The analytical cost alone can range anywhere between two hundred to two thousand dollars per sample, a price that can become overwhelming for any company, big or small, involved in an environmental operation.

Another problem that exists when having to use the services of a fixed laboratory includes the samples aging in unexpected and unknown ways.³ Analytes can evaporate, degrade, chemically react, or undergo a combination of the above during the time between the actual collection of the sample and the analysis of the sample. For each mile or minute that a sample travels or spends unanalyzed, that much more error may be introduced into the final results. In response to these problems, a new environmental technology market

has evolved that focuses on instruments and methods that can be used to generate realtime or near-real-time data and information in the field.

The use of on-site analysis can help reduce many of the problems mentioned above. In many cases, the high hourly cost of a work crew is one hundred times the cost of a mobile laboratory and one thousand times the cost of on-site analytical test kits.³ Field methods have been shown to reduce the times needed to complete an analysis, as well as, being more cost efficient.

The ability of field analysis methods to yield immediate and rapid results without the need for transport, results in major savings in both cost and time, a decrease in the human and ecological risk associated with certain contaminants, and reduces the risk of introduction of error into the final results. As an understanding of the environment as well as data quality needs grew, an increase in the number of plans developed for quick and detailed sampling and analysis also occurred. Screening tools, such as immunoassay test kits, or field-portable instruments, such as portable gas chromatographs or spectrophotometers, have become invaluable in providing rapid data acquisition. This technology has provided the analyst with more rapid, more cost effective, and reasonably accurate knowledge of the site than had previously been possible.

The goal of this project was to develop a simple and inexpensive method for the determination of low levels (2 - 100 ppb) of chromium (VI) in tap water and groundwater under field conditions. The problem with chromium (VI) determination in environmental samples is the reactivity of chromium (III) and chromium (VI).⁴ These two oxidation states of chromium exist in fragile equilibrium. During sampling, storage, and transportation to a fixed laboratory, reduction-oxidation reactions are possible. The

possibility of such a reaction occurring is the major reason why a simple field determination may be more reliable than a sophisticated, and much more expensive analysis in a fixed lab, at a much later time.

Detection of chromium (VI) in environmental samples is important because it has been identified as a toxic compound, causing cancer and skin diseases. The threshold concentration of total chromium in drinking water is 50 ppb.^{4,5} Previously, numerous investigations have been focused on the determination of chromium (VI) in waters at the ppb level under laboratory conditions. They included chromium (VI) pre-concentration and/or separation from chromium (III) in combination with UV-VIS Spectrophotometry, atomic absorption spectroscopy (AAS) or ion exchange chromatography (IEC) determination.

There are kits on the market today for the on-site determination of Cr(VI) in water. These kits are based on the reaction between Cr(VI) and 1,5-diphenylcarbazide (DPC) in the aqueous phase followed by colorimetric determination of the complex formed. The problem with these kits is that they are only able to detect relatively high concentrations (100 ppb and more), which does not meet the standards for drinking water that have been set by the World Health Organization and the US Environmental Protection Agency. This is why new field methods for Cr(VI) detection in waters at low ppb levels are needed.

In natural water, chromium (VI) exists as CrO_4^{-2} and $HCrO_4$ anions. It is possible to concentrate it from water on anion-exchange membranes or resins. These can be treated with a specific colorimetric reagent, diphenylcarbazide. The red complex which is formed can be evaluated by eye and compared with a colorimetric scale, or can be

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measured with a portable colorimeter. The intensity of the color is proportional to the concentration of chromium (VI) that is absorbed on the membrane or resin. Studies were done to develop a fast and simple pre-concentration and determination for on-site chromium (VI) determination in the range of 2-50 ppb in surface, ground and tap waters.

CHAPTER 2

LITERATURE REVIEW

2.1 Aqueous Chemistry of Chromium

Chromium is both an essential nutrient and a toxin to animals and humans.^{5,7} At low concentrations, chromium is thought to play a role in glucose metabolism, as well as, amino- and nucleic acid synthesis. At high concentrations, chromium has been shown to cause nausea, skin ulceration, and lung cancer. At a concentration of 0.1 mg/g body weight, it has been shown to be lethal.⁶

Chromium is a naturally occurring element, the 21^{st} most abundant found in the earth's crust, with an average concentration of 100 ug/g.⁸ Elemental chromium is rarely found in nature, with most of it being contained in ores. FeOCr₂O₃ - Chromite, is the only ore of economic importance. Widespread use of chromium by industry, as well as, the toxicity of the hexavalent form, has caused growing concern about chromium contamination in the environment.

Naturally occurring chromium concentrations in water arise from mineral weathering processes, soluble organic chromium species, precipitation, and sediment load. Industrial use of chromium is the major cause of contamination in the environment. Industries such as steelworks, chromium electroplating facilities, leather tanning plants, chemical manufacturers, wood treatment facilities and chromium mining operations produce high levels of chromium wastes. It has been found that groundwater contamination is almost always the result of industrial processes. Typical concentrations in water range from a fraction of 1 ppb to a few ppb.^{5,8} There are three principal industrial uses for chromium; metallurgical (76%), refractory (13%), and chemical applications (11%). Chromium compounds are used to prevent corrosion, improve product durability, and to manufacture high quality paints. It is also used as a rust and corrosion inhibitor in engines and is added to antifreeze to inhibit corrosion and algae growth. Chromium compounds are also used in chemical research, serving as catalysts for chemical reactions.⁸

Chromium can exist in oxidation states ranging form Cr^{+2} to Cr^{+6} , with Cr^{+3} and Cr^{+6} being the most common. The distribution between chromium (III) and chromium (VI) is regulated by oxidation - reduction reactions. In order for a redox transformation to occur, chromium must be in the presence of another redox couple which can provide the necessary three electrons. In natural aquatic environments, the main significant redox couples are: H_2O / O_2 (aq.), Mn(II) / Mn (IV), NO_2 / NO_3 , Fe(II) / Fe(III), S^{-2} / SO_4^{-2} and CH_4 / CO_2^{-8}

The two major forms of chromium found in natural aquatic systems are chromium (III) and chromium (VI). Figure 1 shows the chromium speciation in groundwater and how it is effected by pE (redox potential) and pH conditions.⁹



Figure 1 pE-pH Diagram for a $Cr-H_2O$ System. Cr activity is 10^{-6}

In less oxidizing environments, chromium (III) is the prevalent species. Under these conditions, chromium (III) exists as Cr^{+3} , $Cr(OH)^{+2}$, $Cr(OH)_3$ and $Cr(OH)_4^-$, depending on the pH . Trivalent chromium behaves as a typical "hard" Lewis acid, and readily forms complexes with a number of different ligands including: hydroxyl, sulfate, ammonium, cyanide, fluoride, and chloride. At a pH above 4, the solubility of chromium (III) decreases drastically. Chromium (III) ions readily precipitate at neutral to alkaline pH values. A pE-pH diagram in natural water may be different because of the presence of various impurities, changes in concentrations, temperatures, etc.. The low solubility of chromium (III) at a pH above 4 is a major reason why it makes up only a small percentage of the total chromium concentration in natural and polluted waters. Chromium (III) tends to be virtually immobile in most groundwater because of its low solubility, and because it is generally adsorbed by clay minerals and soils which typically have high cation exchange capacities at low pH values. Chromium (III) mobility over the entire pH range would probably be enhanced by the formation of complexes due to decreased adsorption or increased solubility of these complexes over the uncomplexed form.⁹

Under natural conditions, manganese oxides are likely to be responsible for most of the oxidation of chromium (III) to chromium (VI).¹⁰ The oxidation reaction occurs in three steps:

- 1) adsorption of chromium (III) onto MnO_2 sites;
- oxidation of chromium (III) to chromium (VI) along with MnO₂ reduction to Mn (II);
- 3) desorption of the reaction products

In a highly oxidizing environment, aqueous chromium is present in the hexavalent oxidation state. Chromium (VI) is extensively hydrolyzed in water. The dominant chromium (VI) species are the oxyanions $HCrO_4^{-2}$ and CrO_4^{-2} , with the equilibrium between the two species dependent on pH. (Figure 1)

There are no significant solubility constraints on the concentration of chromium (VI) in water. Two mechanisms are thought to control the mobility of hexavalent chromium; 1) chromium (VI) reduction to chromium (III), which is rapidly precipitated or

adsorbed, and 2) adsorption. Chromium (VI), when transported by groundwater, can be transformed to and precipitated as chromium (III) if the water plume enters a highly reducing region. Adsorption of chromium (VI) by clays and soils is low to moderate in natural pH ranges. Chromium (VI) is attracted to positively charged soil and clay surfaces, with adsorption decreasing with increasing pH.¹¹ Little or no adsorption occurs above a pH of 8.5.⁴

Under natural conditions, the transformation of chromium (VI) to chromium (III) occurs as a result of reduction, often by ferrous iron solutions, ferrous iron minerals, reduced sulfur compounds, or organic soil matter. ¹¹ These reactions are more likely to occur at low pH values. An example of the role that iron plays in the reduction of chromium (VI) to chromium (III) can be seen in the following equation:

$$3 \text{ FeO} + 6\text{H}^+ + \text{Cr}(\text{VI})_{(aq)} \rightarrow \text{Cr}(\text{III}) + \text{Fe}^{+2}_{(aq)} + 3 \text{H}_2\text{O}$$

The reaction goes to completion relatively rapidly, with the rate depending on the pH, temperature and the concentration of the water and the species respectively. The reduction of chromium (VI) by dissolved sulfides is rapid in acidic media (pH = 2-3), but slows down at increased pH values. As mentioned, organic matter, such as simple amino, humic, fulvic acids, and some microorganisms play a part in the reduction of chromium. In these reactions, which are favored under acidic conditions, an intermediate chromium (V) species is produced which decays to chromium (III) within a few days.

Where there are many potential mechanisms for the oxidation of Cr (III) to

Cr (VI), the mechanism for the oxidation of Cr (III) to Cr (VI) in groundwater appears to be limited to oxidation by manganese oxides.¹¹ It is practically impossible to predict the potential likelihood and the rate of redox reactions between trivalent and hexavalent chromium in natural water because of myriad parameters affecting the process.

The mobility of chromium in water depends on its solubility and its tendency to be adsorbed by soil or aquifer materials. These factors, in turn, depend on the water chemistry and the characteristics of the soil or aquifer material in contact with the chromium-containing water.

2.2 Analytical Methods for Cr(VI) Determination in Water

Concentrations of naturally occurring chromium in groundwater, sea water, and surface water vary. It has been reported that in sea water, (Pacific Ocean), the average concentration of total chromium is 0.5 ppb, of which 15% is Cr (III), 25% is Cr (VI), and 60% is organically bound chromium.^{12,30} In river water, it has been reported that the concentration range of total chromium is 1-10 ppb.^{12,30} The concentration range of total chromium is 1-10 ppb.^{12,30} The speciation of total chromium in municipal water has been reported as 0-35 ppb.^{12.30} The speciation of chromium in river and municipal waters is not usually known.

Currently, methods exist which can be used for chromium (VI) speciation and determination in water. The most frequently used methods are spectrophotometry (colorimetery), graphite furnace atomic absorption spectroscopy (GFAAS), including a separation step, and ion-chromatography (IC).

The analysis of Cr(VI) by spectrophotometry is very common. This test method has been used successfully with reagent grade waters Types I, II, III, tap water, 10% NaCl solution, treated waste water which meets NPDES permit requirements, EPA-extraction procedure leachate water, process water, and lake water.^{12,13} The most popular and reliable colorimetric method is based on the formation of a complex resulting from the reaction of 1,5-diphenylcarbazide (DPC) with chromium (VI) under acidic conditions. The complex forming reaction is pH dependent, with the optimum values ranging from 1 - 2.4. If the pH value is lower then 1, the maximum absorbance value will not be reached. If the pH is higher then 2.4, the maximum absorbance value is reached but at a much slower rate. The following reaction scheme has been deduced for the reaction between Cr(VI) and DPC.

> $2 \operatorname{Cr} (\operatorname{VI}) + 3 \operatorname{DPC} \rightarrow 2 \operatorname{Cr} (\operatorname{III}) + 3 \operatorname{Diphenylcarbazone}$ Cr (III) + Diphenylcarbazone \rightarrow Cr (III) - Diphenylcarbazone

The Cr(III) - diphenylcarbazone complex is responsible for the violet color that forms, with the intensity of the color being proportional to the concentration of chromium (VI) in solution. The absorbance of the colored complex is then measured at 540 nm. The reaction between chromium (VI) and diphenylcarbazide has been extensively

studied.^{14,15,32,33,34} It was reported that chromium (VI) formed colored complexes with both diphenylcarbazide and diphenylcarbazone, but that chromium (III) did not react. It was later reported that Cr(III) and diphenylcarbazone reacted in water, but only very slowly. This reaction is very sensitive, having an absorptivity of about 40,000 L/g cm at a

wavelength of 540 nm.¹² It has been determined that this test method is applicable in the range of 5 ppb to 500 ppb chromium (VI).

The diphenylcarbazide reaction is very specific to chromium (VI). Chromium (III) does not interfere in the reaction, but Fe(III), V(V), Cu(II), nitrite, sulfide and sulfite do. ¹³ Iron and Vanadium at concentrations of 5 mg/L can cause a 10-30% reduction in the recovery of chromium. Copper at a concentration of 100 mg/L yields a reduction of 20-30% in the recovery of chromium in the presence of sulfate. Nitrite concentrations in excess of 10 mg/L as NO₂ yield low test results as well. Sulfide and sulfite reduce chromate in an acid medium which will also give low results.¹² To solve these problems, procedures have been developed to aid in removing the interference without affecting the concentration of Cr(VI) in the sample.¹³ Examples of these procedures include a treatment for iron in which it is masked with phosphoric acid or ETDA. Complexes of Vanadium (V) and Cu(II) can be effectively removed by performing an extraction with chloroform. 13 Graphite furnace atomic absorption spectroscopy (GFAAS) is one of the most readily accessible and sensitive analytical techniques for the determination of chromium. ^{δ} It has been widely used for the detection of chromium in environmental samples over the last ten years.⁸ The detection limit for chromium is 0.05 ng/ml for a 20 ul sample size. Speciation between chromium (VI) and chromium (III) is not possible using GFAAS. Only total chromium concentrations can be detected. To solve this problem, various separation methods, including ion-exchange, extraction and co-precipitation have been proposed. Reviews devoted to the determination of chromium and other microelements in natural waters are available in the literature. ^{16,18} Some recent examples of chromium speciation and determination in natural waters are presented below.

A method for the determination of dissolved Cr(III) and Cr(VI) in sea-water was developed based on preconcentration by coprecipitation and GFAAS.¹⁹ The coprecipitation step was performed with Ga(OH)₃ for the determination of Cr(III). To a 500 ml sample of sea-water containing between 20-250 ng of Cr, was added a portion of a previously prepared Ga solution. This was followed by addition of 5 M NaOH, which was added to adjust the pH into a range of 9.3 - 10.0. The resulting Ga(OH)₃ precipitate which was formed was allowed to settle for about one hour, and then centrifuged for 20-30 minutes. The precipitate, which contained the Ga(OH)₃ and the coprecipitated Cr was separated from the supernate and dissolved in 250 ul of concentrated HNO3 and diluted with water to a volume of 5 ml. The resulting solution was then analyzed by GFAAS. For the total chromium determination, an identical sample was treated with hydroxylammonium chloride for the reduction of Cr(VI) to Cr(III). This was followed by the same co-precipitation procedure described above. The concentration of Cr(VI) could then be determined by the difference between total and trivalent chromium. The detection limit for Cr in the pre-concentrated sample was determined to be 2 ppb, which corresponds to 0.02 ppb detection limit in the initial sea-water sample.

Another AAS technique for the determination of Cr(VI) was developed by Posta et al.³⁶ The technique consist of high-performance flame atomic absorption spectrometry for automated on-line separation and determination of Cr(VI)/Cr(III) and preconcentration of Cr(VI). This method uses a HPLC integrator at the output of the flame AA which allows for the simultaneous determination of both Cr(VI) and Cr(III).

In this method, a HPLC pump is used to deliver the sample into the AA. In between the AA and the HPLC pump, an additional HPLC column (C-18 RP column) was added. This makes the separation of the two oxidation states of chromium possible. The column makes an on-line trace element preconcentration/matrix separation analysis possible. The detection limit was reported to be 0.5 ppb for a 5 ml sample.

A method developed by Beaubleu et al., ⁴ allows for the selective determination of chromium in freshwater samples, with detection limits of 0.021 ppb for Cr(III), 0.004 ppb for Cr(VI) and 0.008 ppb for colloidal/organic chromium. In the speciation step, a 500 ml sample was introduced into a cartridge containing an ion-exchange resin (sephadex DEAE A-25, weak basic anion exchanger). The Cr(VI) and the colloidal/organic chromium would bind to the resin due to their negative charge, while the Cr(III) passed through the column and into a receptor bottle, ready to be analyzed. The cartridge, containing the Cr(VI) and the colloidal/organic chromium was vacuum drained, and 1.5 ml of 5% hydroxylamine hydrochloride was added to elute the Cr(VI). To elute the colloidal/organic chromium, 1.5 ml of 4 M HNO₃ was passed through the cartridge. These samples were then analyzed by GFAAS.

Ion Chromatography, (IC) with post-column reaction of Cr(VI) with DPC has been developed for hexavalent chromium determination in natural waters. ¹² IC is an efficient method of separating ions in a column containing anion or cation exchange resin. Ion chromatography provides a means of separating chromium (VI) from other species present in the sample, many of which interfere with other detection methods. The combination of ion-exchange separation, with a sensitive colorimetric detection method, provides a selective and sensitive analytical method for the determination of chromium (VI) at low ppb levels, with minimal sample preparation. The instrumental setup includes a reagent delivery module and a mixing tee, which is a device that is capable of mixing the eluent stream containing the chromium (VI) and the diphenylcarbizide.¹² The reagent delivery module is used to deliver the color forming reagent, (DPC) into the mixing tee. The chromium (VI), treated with 1,5-DPC, forms a red-violet complex, and is passed through the photometric detector to be analyzed. By virtue of the chromatographic separation, essentially all interfering species are removed before detection.¹²

Other, less frequently used methods have been developed to determine chromium (VI). These include gas-liquid chromatography (GLC), high-performance liquid chromatography (HPLC), and adsorptive stripping voltametric analysis (AdSV).

In GLC, it is necessary for the chromium to be converted into a volatile chelate.⁸ After separation on the column, the chromium can be detected with an electron-capture detector, microwave-excited emission, atomic absorption or mass spectrometry. This method offers good specificity and low detection limits of 0.1 nanograms.

Reverse phase HPLC can be used to detect chromium (VI) in samples. In reverse phase HPLC, a non-polar stationary phase is used along with a polar mobile phase. The detection of chromium (VI) is done based on the formation, separation and oxidation of dithiocarbamate complexes with electro-chemical detectors. ⁸ An absolute detection limit of less than 1 ng has been obtained.

Adsorptive stripping voltammetry (AdSV) has been developed for the determination of chromium (VI) in environmental samples.¹⁵ Stripping analysis occurs in two steps. The first step is deposition, in which the chromium is pre-concentrated onto the working electrode. In the second step, the accumulated metal is measured by applying an anodic potential scan and monitoring the resulting peak currents. The detection limit of this method was found to be 1 ppb. This method has been reported to have high sensitivity and high precision.

The use of the above methods for the field determination of Cr(VI) at low ppb levels is not feasible. The classic spectrophotometry method is capable of being used in the field but only concentrations above 50-100 ppb can be measured without preconcentration. The GFAAS, IC, HPLC, GLC and AdSV methods are all capable of low ppb Cr(VI) determinations, but these methods all require specific preconcentration and/or a separation step which is not easy to perform on-site. As a rule, instrumentation for the above mentioned methods is not field portable. Qualified personal, and a power source are also required. In the field, a mobile laboratory would be required for use of these methods, which adds to the cost and time needed to complete the analysis. Another problem would occur when analyses have to be done in remote areas, which a mobile laboratory would have difficulty getting to.

In this study, a field method for the determination of chromium (VI) in water at low ppb levels was proposed and investigated. Studies were done to develop a combination of preconcentration, using anion-exchange membranes or resins and a determination procedure for the analysis of chromium (VI). The chromium (VI) would be sorbed to the solid support and then treated with 1,5-diphenylcarbazide, forming a rose colored complex upon reaction. A battery operated, portable colorimeter was used to make field measurements possible. Sensitivity, selectivity and precision were evaluated to ensure the usefulness of the method to provide accurate and usable results in the field.

2.3 Solid-Phase Spectrophotometry

Solid-phase spectrophotometry (SPS), is a combination of preconcentration and determination based on the direct measurement of solid phase absorbance after sorption of elements onto it from the solution. SPS has become more popular during recent years. Reasons for this include its simplicity, rapidity, ease of automation, and low detection limits. These properties have made it a very valuable method for the analysis of environmental waters.^{16,17}.

Solid supports can include fine beads of styrene and divinylbenzene anion and cation exchangers, combinations of them, sephadexes, polyvinyl chloride membranes, cellophane and silica. ¹⁶ Particularly important for the photometric determination in SPS is the uniformity of the suspensions and the uniformity of the distribution of the analyte on the solid phase. The concentration step is carried out under static conditions with vigorous mixing of the fine solid material with the solution being analyzed or in dynamic systems by passing sample through a sorption medium.

There are three ways in which preconcentration of the analyte on the solid phase can be completed. ²⁴ The method of choice would depend on the properties of the analyte and organic reagents used. Method 1: The ion-exchanger or other solid support is added to the sample solution together with the chromogenic agent. The complex formed is sorbed under static conditions on the ion-exchanger or passed through an ion-exchange

membrane. Method 2: The analyte is first sorbed on the ion-exchanger or membrane from solution and then the chromogenic agent is added. Method 3: The chromogenic agent is pre-sorbed on the solid sorbent before it is exposed to the sample.

Fine ion-exchangers 50-200 um (100 - 400 mesh) are frequently used as a solid phase. After sorption of the analyte, they are separated from the solution. Some of the ion-exchanger containing the colored sample species is packed as a slurry into a narrow (usually 1 mm) glass or quartz cell. The cell containing the ion-exchanger is placed in a spectrophotometer (colorimeter) and the light transmitted through the cell is measured.

Yoshimura has introduced the term "attenuance" instead of "absorbance", ¹⁸ because in the solid-phase layer, both absorption and scattering of light contribute to the analytical signal. The overall attenuance, A, of the sample layer is given by:

 $A = A_{RC} + A_{SOL} + A_{R} + A_{RL}$

Where: A_{RC} = Absorbance of the complex in the sorbent phase

 A_{SOL} = Absorbance of the solution present between the sorbent particles

 A_{R} = Background arising from light scattering and absorption by sorbent

 A_{RL} = Absorbance of the unbound reagent in the sorbent phase

A_{SOL} may be disregarded when the sample components are very strongly bound so that the ratio of bound to free analyte is very large.

Ideally, A_{RC} can be found by direct measurement of the adsorption at the characteristic wavelength of the element of interest relative to the absorption of identically

prepared ion-exchanger blank, in which the only difference is that the sorption of the analyte was not carried out. In general, however, complete cancellation of the background attenuance cannot be expected, and it is more reliable to compare the difference (ΔA) between the values measured at the wavelength characteristic of the colored species and at a wavelength at which the sample species does not absorb.²⁴ If $A_{RL} = 0$,

then;

$$\Delta A = \Delta A - \Delta A_{\text{blank}} = A_{\text{RC}} + (A_{\text{R}} - A'_{\text{R}}) - (A_{\text{R} \text{ blank}} - A'_{\text{blank}})$$

where attenuance at the non-absorption wavelength is identified by the prime notation

If the packing is similar, the ion-exchanger background spectra should be identical. Therefore;

$$(A_{R} - A'_{R}) - (A_{R ref} - A'_{R ref}) = 0$$
 and: $\Delta A = A_{R}$

2.4 Sensitivity

The sensitivity of SPS determinations can be estimated from the following equation;²⁴

$$A_{RC} = \varepsilon_{RC} l_R C_{RC} = \varepsilon_{RC} l_R C_o V [mv (1 + V/Dm)]$$

where:

 $\varepsilon_{\rm RC}$ = molar absorptivity of the sample species in ion-exchanger phase $l_{\rm R}$ = the mean light-path length through the solid-phase $C_{\rm RC}$ = concentration of the sample species sorbed $C_0 = initial$ concentration of the sample

V = the equilibrated ion-exchanger volume per unit mass

D = distribution ratio of the sample component in ml/g

m = mass of ion-exchanger

v = volume of sample solution

High sensitivity is attained when the values of ε_{RC} , V, m, v, D, and l_R are large.²⁴ In general, a sensitive reagent for conventional solution spectrophotometry may be satisfactory for use in the ion-exchanger method. This would only hold true, however, if the resulting complex is strongly retained by the ion-exchanger.

In a heterogeneous method, the sensitivity depends on the volume ratio of the phases. 24 Using a high V/mv ratio leads to enhancement of sensitivity. Therefore, it may be desirable to use just enough ion-exchanger to provide the sample layer in the cell. The use of large sample volumes increases the time required for equilibration, making the practical limit only a few liters. 24

The sensitivity of this method can be improved in several ways. The amount of ion-exchanger and volume of solution can be optimized, thereby improving the results. The thickness of the sorbent layer can be increased to help improve sensitivity, however, the thicker the layer is made, the larger the background error becomes. The optimal cell size should be chosen so that the increase in background error has a minimal effect. In SPS, a layer of 0.1 cm thickness is more sensitive than ordinary spectrophotometric methods using the same analytical reactions in solution.

These preconcentration techniques make it possible to improve the sensitivity of a determination by a factor of approximately 100 compared to ordinary spectrophotometry performed in solutions.¹⁷

Ions which may interfere in conventional spectrophotometric methods may be effectively eliminated by preconcentrating the analyte on a solid phase and performing SPS. An example of this would be the determination of Cr(VI) using anion-exchange resins opposed to the conventional solution method. In the solution method, Fe(III) present at concentrations of 5 ppm yields a 10-30% reduction in the recovery of chromium.¹¹ If anion-exchange resin were used, Fe(III) would not be adsorbed, and would not interfere in the chromium determination on the solid phase.

It might be expected that the reproducibility of a method that includes the measuring of the absorbance of a solid phase would be much worse then that of solution spectroscopy. However, it can be seen from literature data presented in Table 1 that reproducibility of ion analysis by SPS is good, especially for measurements at the ppb level.²⁴

Element	Conc. in mole/L	# of Sample	Volume	Relative	Ref.
				Error	
Cr (VI)	1x10 ⁻⁷	10	1000	.384 ± .013	14
Cu(II)	7.9x10 ⁻⁹	5	1000	.162 ± .011	28
Zn(II)	1,1x10 ⁻⁶	10	1000	.330 ± .023	31
Bi(III)	8.9x10 ⁻⁸	5	1000	.083 ±.004	30
U(VI)	1.7x10 ⁻⁶	3	200	.432 ± .020	27

However, to achieve good accuracy, cuvettes with a sample and standard should be filled uniformly. This can be verified by absorbance measurements at a wavelength where the sample species does not absorb. If the cuvettes are filled uniformly, the readings at this wavelength should be the same for the sample and standard. When this precaution is taken, the accuracy is comparable to solution methods.

There are many advantages in using SPS. The concentration step makes it possible to determine very low levels (less than 1 ppb) of analyte. When compared to the conventional solution method, the detection limit, as well as, the selectivity of the determination is improved. SPS is especially promising in the analysis of environmental samples for trace metals because the method simplifies the analytical scheme and minimizes the effect of the major components on the determination. Table 2 gives examples of the application of SPS for the analysis of natural waters.

Solid-Phase	Complex	Method of	Reference
	Reagent	Sorption*	
Dowex 50W-X2 H^{+} form100-200	DPC	Complex	13
mesh		Sorbed	
Dowex 50W-XH ^{$+$} form	1,10-phenant-	Complex	25
200-400 mesh	hroline	Sorbed	
Dowex 1-X2Cl ⁻ form 100-200 mesh	NH₄SCN	Complex	13
		Sorbed	
Dowex 1-X8Cl form	Zincon	Analyte	31
100-200 mesh		Sorbed	
Dowex 1-X2 Cl ⁻ form	Zincon	Reagent	13
100-200 mesh		Sorbed	
QAE Sephadex A-25-Cl	KI	Complex	30
		Sorbed	
QAE Sephadex A-25-Cl	NH ₄ SCN	Complex	27
		Sorbed	
Dowex 50W-X4H ⁺ form	PAN	Complex	26
200-400 mesh		Sorbed	
	Solid-Phase Dowex 50W-X2 H ⁺ form100-200 mesh Dowex 50W-XH ⁺ form 200-400 mesh Dowex 1-X2Cl ⁻ form 100-200 mesh Dowex 1-X2 Cl ⁻ form 100-200 mesh QAE Sephadex A-25-Cl QAE Sephadex A-25-Cl Dowex 50W-X4H ⁺ form 200-400 mesh	Solid-Phase Complex Reagent Reagent Dowex 50W-X2 H ⁺ form 100-200 DPC mesh 100-phenant- Dowex 50W-XH ⁺ form 1,10-phenant- 200-400 mesh hroline Dowex 1-X2Cl ⁺ form 100-200 mesh NH4SCN Dowex 1-X8Cl ⁺ form Zincon 100-200 mesh Zincon 100-200 mesh KI QAE Sephadex A-25-Cl KI QAE Sephadex A-25-Cl PAN 200-400 mesh PAN	Solid-PhaseComplexMethod of ReagentDowex 50W-X2 H* form100-200DPCComplexDowex 50W-X2 H* form100-200DPCComplexDowex 50W-XH* form1,10-phenant-Complex200-400 meshhrolineSorbedDowex 1-X2CI* form 100-200 meshNH4SCNComplexDowex 1-X8CT formZinconAnalyte100-200 meshZinconReagent100-200 meshSorbedSorbedDowex 1-X2 CI* formZinconReagent100-200 meshSorbedSorbedQAE Sephadex A-25-CIKIComplexQAE Sephadex A-25-CINH4SCNSorbedDowex 50W-X4H*formPANComplex200-400 meshPANSorbed

 Table 2 SPS Application for the Determination of Metals in Natural Waters

* For descriptions of the different methods of sorption, see page 14
It is seen from this table that the complexing reagents usually applied in SPS methods are the same as those used for conventional determinations in solution (e.g. 1,5-DPC for Cr(VI), 1,10 phenanthroline for Fe(II), etc.). However, the sensitivity of SPS for the same ions and reagents is much higher. This is achieved because of the effective combination of preconcentration and determination directly on the solid phase.

In comparison with conventional ion-exchange preconcentration of metal ions, involving sorption on a column followed by elution, the SPS method is much faster. First, ion-exchange in static conditions is faster than preconcentration in a column. Secondly, elution of sample from a column is time consuming and requires expensive, high purity reagents. An additional advantage may be increased selectivity of the determination due to the preconcentration step. SPS does not require expensive equipment or a professional laboratory staff. After minimal training, a technician can learn the determination of a certain analyte using the SPS method. For these reasons, SPS is an especially promising technique for on-site analysis of environmental samples.

2.5 Cr(VI) Determination by SPS

Although qualitative methods of metal determination on an ion-exchange resin were known earlier, Yoshimura and co-workers first developed quantitative determinations using the SPS method, and measured Cr(VI) in aqueous solutions at ppb levels.¹³ The Cr(VI) - DPC complex, in acid media, was adsorbed on a fine cation exchange resin (Dowex 500W-X4, 100-200 mesh) under static conditions. The colored resin was collected and, as a slurry, transferred to a 1 mm cuvette. A double beam UV-VIS spectrophotometer was used for the analysis. A perforated metal plate was used as a

neutral density filter in the reference beam to balance the light intensities. The absorbance value depends on the analyte concentrations, but also on the packing of the resin due to the change in path length or scattering behavior in the cell. To correct these interferences, absorbance readings were taken at two different wavelengths, 550 and 700 nm. The maximum absorbance of the colored Cr(VI) - DPC complex is at 550 nm, and at 700 nm, the complex does not absorb. The difference of these readings served as an analytical signal. Later this method was developed for Cr(VI) determination in natural water. ¹⁴ To a one liter sample containing 0.52-15.5 ppb of chromium (VI), concentrated sulfuric acid was added to make the concentration of acid approximately 0.05 M. Then, 15 mls of 1,5-DPC/0.25% acetone solution and 0.5 grams of the same cation exchanger were added. The solution was stirred for 30 minutes. Measurements were carried out in a 1 mm cell at 550 and 700 nm using a UV-VIS spectrophotometer. It was reported that this method was reliable in the concentration range of 0.5 ppb - 15.6 ppb. The precision was found to be 4-7% for 10 measurements depending on Cr(VI) concentrations. Vanadium (V), iron (III) and molybdenum (VI), which interfere in the conventional method did not interfere when present in up to 100 times the concentration of chromium (VI). It was reported that some ions did interfere with this Cr(VI) determination. For example, 1 ppm Cu(II) reduced the absorbance by 30%. The influence of some important ions, especially Ca, and Mg, was not reported, although they are present at high levels in natural waters and can compete with the Cr(VI) - DPC complex for sites on cation-exchanger resin.

Another variant of the Cr(VI) determination by SPS was proposed by Ohzeki, Sakuma, and Kambara. 20 They used a mixture of very fine (30-50 um) strong cation and anion exchangers in order to accelerate sedimentation or filtration of the solid phase.

A 100 ml sample of the solution containing less than 1.0 ug of chromium (VI) was placed into a separatory funnel with 10 ml of 0.1M H₂SO₄, a mixture of anionic and cationic resin at a 3:1 ratio, and 1.0 ml of 0.4% 1.5-DPC solution. The funnel was shaken for 12 minutes and the resin was filtered out with filter paper. A disk of colored resin, 17 mm diameter and about 3 mm in thickness, was formed. The disk was dipped into a dilute acetate buffer solution of pH 4.8 for 10 seconds in order to stabilize the coloration. Another disk of resin was prepared in pure water and used as a reference. The filter strips were fixed on a glass plate and the reflectance readings were taken at 550 and 700 nm. The net reflection was obtained from the difference of the two readings. The sensitivity of this method was reported to be about 100 times higher than ordinary solution methods. It was found that Cr(VI)-DPC recovery decreased considerably with the addition of CaCl, in low ppm levels, which is attributable to the competition between the cations of Cr(VI)-DPC complex and Ca^{+2} ions for the cation exchange sites in the mixed resin. To reduce the influence of interfering ions, the extraction of chromium (VI) with tributylphosphate followed by back extraction into water was suggested.

In another SPS method, the determination of Cr(VI) was carried out by the sorption of the analyte on an anion-exchanger, followed by the reaction with a colorimetric reagent. ²¹ A 0.5-1 liter sample, at a pH of 4-6, was mixed with 0.2 grams of a strong basic anion-exchange resin (200-400 mesh). The ion-exchanger was agitated with nitrogen bubbles for 20 minutes and was separated from the sample in 1 minute by flotation with the addition of an anionic surfactant. The resin was then collected, rinsed, and treated with 1 ml of a 1% KI solution at a pH = 1. The resin became a yellowish-brownish color, with the intensity depending on the concentration of chromium (VI) on

the ion-exchanger. A 1 mm cuvette was filled with the ion-exchanger beads and the measurement was made at 440 nm. A second identical cuvette was filled with resin, treated with water and KI and used as a blank. It was reported that most ions did not interfere significantly and that the whole process took about 40 minutes.

A membrane variant to the SPS method for Cr(VI) determination in water was developed by Savvin et al.^{22,23} The chromium (VI) was preconcentrated by sorption under dynamic conditions on a specially prepared polyacrylonitryl membrane. The solution being analyzed was passed through the membrane at a rate of 10 ml/min. for two to ten minutes, depending on the concentration of chromium (VI) present. The membrane, which was initially white, was then treated with a 0.025% aqueous-acetone solution of 1,5-DPC, turning it a pink color. The intensity of the color was proportional to the concentration of chromium (VI) sorbed on the membrane. The diffuse reflectance of the membrane was measured at 560 nm. The detection limit was estimated to be 0.5 ppb for a ten minute sampling time.

Savinn et all proposed another method for the determination of Cr(VI) by SPS. In this method, the Cr(VI) was preconcentrated on a disk of polyacrylonitrile fiber, 20 mm in diameter, which had been filled with a strongly bound anion-exchanger (AV-17 anionexchanger containing -N(CH₃)₃Cl active groups). It was found that the greatest response was achieved when the mass of the disk was greater than 22 mg.

Solutions of Cr(VI) were passed through the disk at a rate of 10 ml/min. and then treated with a 0.025% solution of DPC in acetone. It was found that the higher the concentration of acetone in the DPC/acetone solution, the more the Cr (VI)-DPC complex was washed off of the disk. It was also observed that the larger the volume of DPC solution passed through the disk, the more the colored complex was washed out. The optimum signal was obtained when a volume of 4 ml was used. After passing the solution through the disk, the disk was allowed to sit for three minutes before it was analyzed by diffuse reflection spectroscopy at a wavelength of 560 nm.

It was reported that this method was valid over the range of 0.002 - 0.05 ppm Cr(VI) in potable, and waste waters. The analysis can be carried out in 15 minutes. The selectivity of this method was determined to be better than the existing methods for determining Cr(VI) by photometry in solution, and ion-exchange colorimetery methods.

Although in the hexavalent chromium determination, a rather high tolerance for interfering anions has been reported, it is clear that some anions present in natural waters at high levels (Cl⁻, HCO₃^{-,}, SO₄⁻²) may interfere with the sorption of Cr(VI) on anion-exchange resins or membranes.^{14,21,22} Among these anions, divalent sulfate ion is the most competitive with Cr(VI) for sites on an anion-exchange material.²⁵

SPS has been applied to the determination of chromium (VI) in water using flow injection analysis. ¹⁸ The method involves introducing the product of the reaction between chromium (VI) and 1,5-diphenylcarbazide into a flow-through cell, in which the light path has been partly filled with a cation exchanger. As the solution is passed through the cation exchanger, the chromium-DPC complex is sorbed onto the resin and its absorbance measured by a photometric detector. For fresh water samples, an appropriate sample size was passed through a pre-treatment column, (a cation-exchange cartridge column packed with BioRad AG50W-X8 cation exchange resin in the hydrogen form). This was done to remove any cations which might cause a change in the background absorbance. An 8 ml

aliquot of the sample was combined with 0.2 ml of a 3 M H_2SO_4 solution, and 0.2 ml of the DPC solution and diluted to 10 ml with water. Immediately after mixing, 4.4 ml of the mixture was introduced into the flow injection stream containing a carrier solution comprised of 20 ml of the 1 to 5 H_2SO_4 solution and 20 ml of acetone diluted to 1 L with water. The attenuation was continuously measured at 550 nm. The concentration of Cr(VI) was determined by the use of a previously prepared calibration curve. After every four sample runs, a desorbing solution, comprised of 3 M HNO₃ was introduced into the stream to clean out the flow injection system.

For saline waters, i.e. sea water, an absorbance increase was measured as the difference between the sample absorbance and the constant background absorbance of the sample. The Cr(VI) concentration was determined by means of a calibration curve prepared by using standards having a similar electrolyte composition to that of the sample solution. This method produced results that were about 160 times more sensitive than that of the solution method. The precision was measured with 4.4 ml sample solutions containing 2.2 ng of Cr(VI). In six determinations, the relative standard deviation was 4.3% The detection limit was determined to be 0.33 ppb with a sample size of 14.3 ml. Without preconcentration, this method is directly applicable to the analysis of natural water samples containing chromium (VI) at less than 1 ug/dm⁻³. ¹⁸

These methods for the determination of Cr(VI) at ppb levels by SPS were not focused on field applications. The problem with sorption of Cr(VI)-DPC complex on cation-exchange materials is the interference of some cations. To avoid such interferences, additional operations such as ion-exchange pre-treatment are needed which makes the methods more complicated, and less suitable for field use. To carry out flow injection analysis in the field requires at least a specially equipped mobile laboratory and qualified personnel.

The purpose of this investigation was to develop a simple, inexpensive, and reliable method for on-site Cr(VI) determination or screening in surface, ground, and tap waters at low ppb levels. Several methods using commercial anion-exchange membranes and resins have been studied.

CHAPTER 3

EXPERIMENTAL PROCEDURES

3.1 Water Sample Characteristics

The experiments were carried out with three different types of water: 1. Deionized water, 2. Tap water and 3. Groundwater. The deionized water was produced by the DI system in the Otto York Environmental Center, located on the New Jersey Institute of Technology campus. Two different tap water samples were analyzed, one from Newark, NJ and the other from Flanders, NJ. The groundwater samples were taken from two different wells, one located in Green Township, Sussex County, New Jersey, and the other from Effort, Monroe County, Pennsylvania. The tap and groundwater samples were stored at 4° C for up to five days. Some characteristics of the tap and groundwater samples are presented in Table 3.

 Table 3 Characteristics of Water Samples

Water Sample	pН	[SO ₄ ⁻²] ppm	$[SO_4^{-2}]$ ppm by IC	Total Cr
				ppb
Tap Newark	6.7	50-100	60	1.9
Tap Flanders	6.4	<10	2.4	1.3
Grd. Green, NJ	6.1	<10	9.8	<1.0
Grd. Effort, PA	7.6	25-50	40.7	<1.0

The pH was measured using an Orion model # 420A pH meter. Total Cr was measured by GFAAS. The groundwater was first filtered through a 0.45 um membrane filter. The natural concentration of Cr(VI) in the water samples was found to be <0.5 ppb. This was determined by evaporating a 100 ml portion of the water sample to 10 ml. A semi-quantitative analysis was then carried out with the use of anion-exchange resin and SPS. The method used for this analysis is discussed in detail below.

Since sulfate levels were found to be important in the analysis, a screening test was developed. Ten ml of a 1000 ppm BaCl₂ solution was added to 10 ml of a water sample. The mixture was shaken for 1 minute and allowed to stand for five minutes. The turbidity of the solution was then compared, by eye, to previously prepared standards of 200, 100, 50, and 10 ppm SO_4^{-2} . This sulfate screening test provided the ability to classify samples into ranges of sulfate concentrations of > 200 ppm, 100-200 ppm, 50-100 ppm, 10-50 ppm and < 10 ppm of sulfate ion.

To verify the results from the screening test for sulfate, the samples were analyzed by ion chromatography. (Model A-102 Waters, Eluent - Borate/Gluconate, Column IC-PAKA HC (Waters), Conductivity detector - Waters 431 @ 35°C, Pump - Waters 600E). A calibration curve was prepared with standards of 10, 20, 30, 50, and 100 ppm sulfate. The samples, in duplicate, were then injected into the IC. It was found that the screening test and the IC analysis matched closely. The use of the IC provided more accurate sulfate values which gave a better idea of the capacities of the membrane and the resin to tolerate sulfate ions.

3.2 Reagents

Hexavalent chromium was added to the samples artificially before analysis. A 1002 ppm, solution of $NH_4(Cr_2O_7)$ in 2% HNO₃ (Inorganic Ventures, INC.) was used as the source of Cr (VI). After some preliminary experiments and unsuccessful attempts to get a highly selective commercial membrane specially developed for Cr(VI) sorption from water, a 47 mm diameter, strong basic anion-exchange membrane filter, (SB-6407 Acropor Ion-exchange membrane; Gelman) was chosen for Cr(VI) preconcentration. The membrane has quartenary ammonium active groups attached to a cross-linked polystyrene divinylbenzene lattice. The disk have a thickness of 152 um, and are supplied in the chloride form. The ion- exchange capacity ranges from 0.08 - 0.20 meq per disk.

A strong anion exchange resin, Dowex 1 X 8, with bead sizes of 100-200 and 200-400 mesh (Fluka), was also used for Cr(VI) preconcentration. The Dowex 1 x 8 resin has trimethylbenxyl ammonium active groups, with an ion-exchange capacity of about 1.2 meq/ml and is supplied in the chloride form.

Other reagents used in this investigation include 1,5-diphenylcarbazide (DPC) (Fluka), concentrated sulfuric acid (Fisher), acetone (Fluka), $BaCl_2$ (J.T. Baker), Na_2SO_4

(Fisher), NaNO₃, NaHCO₃, and NaH₂PO₄ all distributed by Fluka. All of the reagents were of analytical grade. The color development reagent was a 0.04% DPC solution. It was prepared by adding 500 mg of the DPC to 25 ml of acetone. Two ml of the DPC-acetone solution was then transferred to a 100 ml volumetric flask containing 10 ml of 1 M H₂SO₄. The flask was filled to the mark with DI water. This solution was made fresh every day before use. BaCl₂ and Na₂SO₄ were used to develop the sulfate screening test, and NaNO₃, Na₂SO₄, NaHCO₃, and NaH₂PO₄ were used to make solutions of ions to be tested as possible interference with Cr(VI) sorption on the ion-exchange materials.

3.3 Preconcentration of Cr(VI) from Water Samples

3.3.1 Sorption on Membrane

Two different methods were used to sorb the Cr(VI) onto the membrane. In the first of them, a 1000 ml vacuum filter flask (Millipore) was used to pass the sample through the membrane. The rate of filtration was controlled by a clamp. One hundred milliliter water samples, which had been previously filtered through a 0.45 um filter (Millipore) to remove any suspended solids, were spiked with the Cr(VI) solution, giving concentrations of Cr(VI) ranging from 5-50 ppb. The samples were passed through the membrane at different rates.

In the second set of experiments, a method was devised which would be applicable for use in the field. A 120 ml plastic syringe and a membrane holder (Millipore- Swinnex-47) were used. The anion-exchange membrane was placed inside the holder where it was held in place by a threaded collar. The holder was then connected to the syringe. One hundred milliliters of the sample was added to the syringe. The plunger was put into the syringe and the sample was slowly pushed through the membrane at a rate of 25.0 ml/minute.

3.3.2 Sorption on Anion-Exchange Resin

Two methods were used to sorb Cr(VI) on the anion-exchange resin beads. In the first method, a 500 ml sample, containing 5-50 ppb of Cr(VI), and 0.45 grams of the anion-exchanger were mixed in a beaker and stirred for 30 minutes at low speed with a magnetic stirrer.

In the second set of experiments, a method was devised that would be more applicable for use in the field. A 1-liter polyethylene terphthalate (PET) soda bottle was used instead of the beaker to contain the sample. The bottle had been modified by the addition of a small plastic tube through which the bottle could be drained without removing the cap. Another variant was the use of a plastic ketchup bottle, which contained a flip top lid in place of the soda bottle. A piece of filter paper was placed inside the lid which allowed the water to be squeezed out while retaining the resin inside the bottle's cap.

A 500 ml sample, containing 5-50 ppb Cr(VI) and 0.45 grams of the anion exchange resin were placed in the bottle, capped and shaken for five minutes, then allowed to stand for five minutes. This mixing procedure was repeated three times. Total time of the process was 30 minutes. The bottle was then turned upside-down, to allow the resin to settle into the cap, where it would eventually be collected. The water was drained by removing the cover on the plastic drainage tube or opening the flip top and squeezing until all of the water was expelled, leaving only the resin in the cap. The GFAAS was used to analyze chromium concentrations in the water samples during the sorption process. The model used was a Thermo Jarrell Ash, Smith-Hieftje 12 CTF-188. A FASTAC aerosol deposition module was used to introduce the sample (20 ul) into the furnace. Table 4 details the program recommended by Thermo Jarell Ash for Cr determination in water and used to analyze Cr in this investigation.

	Dry	Pyrolysis	Pyrolysis	Atomization	Clean
Temp (°C)	150	900	1000	2300	2500
Ramp (Sec.)	2	15	15	0	0
Hold (Sec.)	0	0	0	4	2
Purge	1	2	2	0	3

Table 4 Instrumental Conditions for Cr Determination by GFAAS Method

The peak area was measured over a five second interval.

Calibration curves were prepared using a 5, 10, 25, and 50 ppb Cr(VI) solutions in DI water. Linear curves were obtained over this concentration range. The GFAAS was capable of determining at least 1 ppb of total chromium in water samples.

3.5 Colorimetric Analysis of Cr(VI) Preconcentrated on Membrane

After the sorption of the Cr(VI) onto the membrane, the membrane was rinsed with DI water and placed into a plastic beaker. To this was added 5 ml of the 0.04% DPC solution in acetone. They were stirred occasionally by manual swirling for two minutes.

A reddish-pink color began to form on the membrane and then quickly washed out into the solution. After two minutes, the membrane had become colorless and the solution turned a reddish-pink color, with the intensity of the color depending on the Cr(VI) concentration. The solution was placed into a 1 cm cuvette and its absorbance measured with a Varian DMS 200 UV-VIS spectrophotometer at 550 nm. A portable, battery operated, single beam colorimeter (Milton Roy Mini 20 spectrophotometer) for on-site measurements was also used to determine the absorbance of the solution. Standards were made and treated using the same procedure as the samples, to prepare a calibration curve. Concentrations of 50, 25, 10, and 5 ppb Cr(VI) were used. Linear curves were obtained for this concentration range.

3.6 Colorimetric Analysis of Cr(VI) Preconcentrated on Anion-Exchange Resin

Solid phase spectrophotometry (SPS) was the method used to determine Cr(VI) directly on the anion-exchange beads. After stirring the 500 ml water sample and 0.45 grams of ion-exchange beads in a beaker, the resin was filtered from the water sample, rinsed with DI water and put into a plastic beaker. To the beaker was added 10 ml of the 0.04 % DPC solution. The mixture was stirred on a magnetic stir plate for 25 minutes to allow the color to fully develop on the resin, while leaving the solution practically colorless. The resin, as a slurry, was transferred to a 1 mm cuvette by use of a disposable plastic pipette and allowed to settle for five minutes. This was done to ensure an evenly packed resin layer. The sample was analyzed using a Varian DMS 200 UV-VIS spectrophotometer at 550nm. A calibration curve, which had been previously prepared using standards of 5, 10, 25, and 50 ppb Cr(VI), and the above procedure, was used to determine the sample concentrations. The calibration was linear over this concentration range. Absorption of samples and standards was compared at 780 nm. The Cr(VI) - DPC complex does not absorb at this wavelength. This was done to make sure that the cuvettes were uniformly packed.

For the SPS determination using the field method, the resin which had been collected in the bottle cap was rinsed with DI water. The DI water was removed from the cap with a plastic syringe and 5 ml of the 0.04% DPC solution was added. The mixture was allowed to stand for 25 minutes with occasional stirring to allow the color to fully develop on the resin.

A screening test and a quantitative method were developed to be used in the field with the above procedure. A color scale was made using five standards containing 0, 5, 10, 25, and 50 ppb Cr(VI) in DI water. The standards were treated in the same manner as the samples. The color was developed on the resin, and using acrylic paints, a color scale was made on a white background so that a quick comparison by eye could be made to estimate the Cr(VI) concentration in the water samples.

For the more quantitative method, the resin was transferred as a slurry to a 1 mm cuvette and allowed to settle for five minutes. The absorbance was measured by the portable, hand held colorimeter. Absorbance readings were compared to a previously prepared calibration curve in which Cr(VI) solutions of 0, 5, 10, 25, and 50 ppb were prepared. Linear calibration curves were obtained over this concentration range.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Preconcentration and Sorption on Anion-Exchange Membranes

Tests were run to determine a maximum flow rate at which 100% adsorption of Cr(VI) would occur. One hundred ml of DI water, spiked with 50 ppb Cr(VI), was passed through an anion-exchange membrane, SS-47, at various flow rates. By GFAAS analysis of the effluent, it was found that adsorption of Cr(VI) on the membrane was 100% at flow rates up to 50 ml/minute. For Cr(VI) pre-concentration from natural waters, a flow rate of 25 ml/min. was chosen. It was found that practically 100% Cr(VI) sorption was occurring for tap water from Flanders and Groundwater from Effort. However, only 50-65% of the Cr(VI) was sorbed from the tap water from Newark and the groundwater from Green Twp.. It was concluded that these samples contained other anions that were competing for the active sites on the membrane, causing interference with the adsorption of Cr(VI).

The selectivity of the sorption of Cr(VI) was investigated using the anionexchange membrane. Anions that were studied included Cl, HCO_3 , NO_3 , H_2PO_4 , and SO_4^{-2} , because these are commonly found in natural waters. The solutions containing these ions were prepared and studied at concentrations which are usually not exceeded in fresh, unpolluted natural waters.

To a 100 ml sample of DI water was added various concentrations of Cr(VI) and one of the above anions. The sample passed through the membrane at a flow rate of 25 ml/min., and the Cr(VI) in the filtrate was measured by GFAAS. Table 5 shows the effects of the added anions on the sorption of Cr(VI) by the membrane.

Conc. of Cr (VI)	Added Anion	Conc. of Added Anion (ppm)	% Sorption of
(ppb)			Cr (VI)
50	Cl	250	102
50	HCO ₃	250	103
50	H ₂ PO ₄	50	99
50	NO ₃	50	98
50	SO_{4}^{-2}	10	98
50	SO_4^{-2}	15	89
50	SO_4^{-2}	20	81
50	SO_4^{-2}	30	67
50	SO_4^{-2}	50	55
25	SO ₄ ⁻²	25	85
25	SO_4^{-2}	50	40
25	SO_4^{-2}	100	43

Table 5 Effect of Anions on Cr(VI) Sorption by Anion-Exchange Membrane

From the above data, it was found that Cl_{1} , HCO_{3} , NO_{3} , and $H_{2}PO_{4}$ did not interfere with the adsorption of Cr(VI) on the membrane in concentrations usually found

in tap and ground waters. However, SO_4^{-2} severely interfered when its concentration exceeded 10 ppm. One way to overcome the SO_4^{-2} interference would be to dilute the sample, thereby reducing the concentration of SO_4^{-2} below the threshold level of 10 ppm. However, the sensitivity of the Cr(VI) determination in the sample would also be reduced, as this is diluted as well.

Another way to minimize the problem would be to use two stacked membranes simultaneously to sorb the Cr(VI). This would give twice the absorptive capacity. Table 6 shows the results obtained by using 100 mls of 50 ppb Cr(VI) solutions in DI water, tap water and groundwater samples with two stacked membranes.

Sample	Conc. of	% Cr(VI) sorbed
	SO4 ⁻² ppm	
DI	20	99
DI	30	92
DI	50	86
DI	100	50
Green, NJ	9.8	100
Effort, PA	40.7	64.6
Effort, PA	40.7	71.7
(3 membranes)		

Table 6 Sorption of Cr(VI) on Two Membranes





Figure 2 Effect of Sulfate Concentration on the Recovery of Cr(VI) using Single and Double Anion-Exchange Membranes.

It is clear from the graph that a single membrane can not be used for Cr(VI)sorption from water with sulfate concentrations higher than 10-15 ppm. It was found that SO_4^{-2} has a strong affinity for the membrane and competes too strongly with the Cr(VI). It is clear that the use of double membranes is more tolerant to sulfate ions then the use of a single membrane.

The water samples used above were analyzed to determine their concentration of SO_4^{-2} . Ion Chromatography, as well as, the sulfate screening test described in the experimental section, were used for this determination. By IC analysis, it was found that the concentration of sulfate ion for the Flanders and Green Twp. water samples were 2.4 and 9.8 ppm, while the concentration of sulfate ion for the Newark and Effort water samples were found to be 60.2, and 40.7 respectively. The results of the sulfate screening

test compared well to the IC data, with SO_4^{-2} concentrations in the Flanders and Green water samples being <10 ppm while the concentration of SO_4^{-2} in the Newark and Effort water samples were 50-100 and 25-50 ppm respectively.

It was reported in the literature that Fe(III) also causes interference in the DPC-Cr(VI) determination. A 1 ppm solution of Fe(III) was prepared in DI water and spiked with 50 ppb Cr(VI). The solution was passed through a membrane at a flow rate of 25 ml/minute. The filtrate was analyzed by GFAAS and found to contain < 1.0 ppb Cr(VI). In this method of analysis, it was determined that Fe(III) in concentrations of 1 ppm or less, would not interfere in the sorption of the Cr(VI).

4.2 The Effect of pH on Cr(VI) Sorption on Anion Exchange Membranes

The effect of pH on Cr(VI) sorption from DI water was studied. One hundred ml samples of DI water were spiked with 50 ppb Cr(VI), and pH adjusted by the addition of HCl or NaOH. The samples were passed through the membrane at a flow rate of 25 ml/minute and the concentration of Cr(VI) was determined in the filtrate by GFAAS. Table 7 shows the results of this analysis.

Table / Effects of pH on Cr(VI) Adsorption on Membran	Cr(VI) Adsorption on Membranes	r(V.	Ion	ofpH	Effects	ble 7	Т
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pH	% Sorbed
2.8	23
4.3	96
5.2	99
7.0	99
9.9	103

At a low pH, the sorption of Cr(VI) was hindered. This was caused by the conversion of the Cr(VI) to chromic acid, which has a lesser affinity for the anion-exchange membrane. It was found that in the pH range of 5.0 - 10.0, the pH range of natural water, 100% adsorption on the membrane occurred as long as the capacity of the membrane had not been exceeded. Therefore, a normal pH variation in waters to be tested has little effect on the sorption of Cr(VI) on the anion-exchange membrane.

It can be concluded that complete Cr(VI) sorption can be achieved with one anionexchange membrane at sulfate concentrations of less than 10-15 ppm or two stacked membranes at sulfate concentrations of 20-25 ppm. A flow rate of 25 ml/minute was used. With a sample size of 100 ml and a flow rate of 25 ml/minute, the sorption procedure would only take four minutes to complete. This was considered to be an acceptable analysis time for on-site measurements.

The membrane used in these experiments had an ion-exchange capacity of 0.08-0.2 meq per disk. The membrane, in the absence of all other anions, would be able to absorb a maximum concentration of 38 - 96 ppm sulfate in a 100 ml sample. Taking into

consideration that the dynamic capacity is usually two to three times less than the static capacity due to the sorption process not usually reaching equilibrium, it is apparent that the membrane used in this investigation does not provide sufficient capacity to sorb all anions from all water samples.

Ways do exist to increase the amount of Cr(VI) sorbed on the anion exchange membrane. One would be to use a membrane that had a higher ion-exchange capacity. This would increase the membrane's tolerance for anions, sulfate ions in particular, leaving more active sites available for the sorption of Cr(VI). Another way of improving the process would be to use a membrane with the same ion-exchange capacity but with more mass. This would increase the amount of ions capable of being adsorbed per disk, increasing the amount of Cr(VI) that could be sorbed. A membrane more selective towards Cr(VI) sorption would also be a way of improving this technique.

4.3 Elution of the Cr(VI)-DPC Complex from the Membrane

After sorption of the Cr(VI) onto the membrane, the next step was to develop the Cr(VI)-DPC rose colored complex and analyze it by colorimetery. It had been reported in the literature that a dilute DPC/acetone solution could be used to keep the color complex on the membrane for measurement by reflective spectroscopy. Completely eluting the Cr(VI)-DPC complex off of the membrane and measuring its absorbance with a portable spectrometer would make this technique more useable in the field. In the first experiment, a membrane on which Cr(VI) had been sorbed, was soaked in 50 mls of a 0.025% solution of DPC in acetone. The color, as expected, had formed on the membrane, but at the same time, the rose color began to show in the solution It appeared that the Cr(VI)-DPC complex was partially eluting from the membrane. It was thought that more concentrated solutions would help in thoroughly eluting the complex off the membrane. A 0.04% DPC in acetone solution was used and all of the colored complex had washed out of the membrane and into the solution.

Next, the volume of the 0.04% DPC in acetone solution was varied to see if the sensitivity of the method could be improved. Volumes of 25, 20, 10, and 5 ml of the DPC in acetone were studied. As the amount of the DPC in acetone solution decreased, the sensitivity of the method increased. Table 8 shows how the absorbance of the DPC in acetone solution increased as its volume decreased.

Volume of DPC	Absorbance	Absorbance	Absorbance	Absorbance
in acetone	with 50ppb	with 25ppb	with10ppb	with5ppb
solution	Cr(VI)	Cr(VI)	Cr(VI)	Cr(VI)
25 ml	0.099	0.049	0.023	0.011
20 ml	0.163	0.082	0.042	0.020
10 ml	0.306	0.155	0.062	0.033
5 ml	0.597	0.280	0.151	0.063

Table 8 Effect of Variation in the Amount of DPC in Acetone Solution on Sensitivity

Using 5 ml of the 0.04% DPC in acetone solution increased the sensitivity of this method by six times, allowing Cr(VI) levels as low as 2 to 3 ppb detectable.

Calibration curves, (an example of one is shown in figure 3), were prepared with DI water spiked with Cr(VI). A 100 ml sample was passed through a membrane at a rate of 25 ml/min., followed by the soaking of the membrane in 5 mls of the 0.04% DPC in acetone solution. The colored solution was then transferred into a 1 cm quartz cell and analyzed at 550 nm. The linearity of the calibration curve was very good over the range of Cr(VI) concentrations used. The calibration curves were reproducible with correlation coefficients ranging from 0.999 - 1.0.



Figure 3 Example of Calibration Curve

Natural water samples were spiked with known concentrations of Cr(VI) and analyzed. From previous experiments, it had been determined that only the Flanders and The Green Township water samples were low enough in sulfate concentration to be analyzed by the membrane method. One hundred ml of the samples, spiked with various concentrations of Cr(VI), were sorbed and eluted from the membrane as described above. The results are shown in Table 9.

 Table 9
 Cr(VI) Recovery from Spiked Natural Water Samples Using an Anion-Exchange Membrane

Concentration of Cr (VI)	Recovery of Cr (VI) from	Recovery of Cr (VI) from
Added (ppb)	Flanders Water (ppb)	Green Township water
		(ppb)
50	52.7	48.8
25	24.2	24.0
10	9.5	10.9
5	6.1	5.2

This method is easily performed in the field. The time required for analysis, including preconcentration, is under ten minutes. The only equipment required is a syringe, a membrane holder and a portable colorimeter which runs on a rechargeable battery pack. It was found that this method of analysis was able to detect levels of Cr(VI) as low as 2 ppb in natural waters. This is a 20-fold improvement over the current

techniques used to analyze Cr(VI) in natural water. The improvement can be attributed to the pre-concentration step which takes place on the membrane.

This method is very selective for Cr(VI). It has been reported in the literature that a number of different cations can cause interference with the colorimetric determination of Cr(VI). In this method, an anion-exchange membrane is used to sorb the Cr(VI), therefore, cations in the sample pass through the membrane and remain in the filtrate. Some oxy-anions however can also interfere. Species such as Mo(VI) and V(V) can interfere when they are present in higher concentrations. Fortunately, these species are not likely to be present in significant concentrations in natural fresh waters. The method selectivity arises from both the selectivity of the solid phase extraction, which elimimates interfering cations and the reagent. The method is made even more selective with the use of 1,5 Diphenylcarbazide as the colorimetric reagent. This reagent is very specific for Cr(VI), thus eliminating the possibility of interference from several anions that may be sorbed on the membrane. It was concluded that the sulfate ion is the only severe drawback to this method. A membrane material with improved selectivity for Cr(VI) over sulfate is needed. A membrane with a larger ion capacity is also a possible solution to this problem. Further work in these areas needs to be completed.

For waters containing more than the tolerable sulfate levels, another method, using sorption on anion-exchange resin beads rather than a membrane, was developed.

4.5 **Preconcentration on Anion-Exchange Resin**

The greater ion exchange capacity of Dowex 1-8x anion exchange resin was employed to overcome the capacity limitations of the membrane ion exchangers. Test were done to

determine the amount of time required for 100% adsorption of Cr(VI) to occur on the ionexchange resin. A 500 ml sample of DI water, containing 50 ppb Cr(VI) was stirred with 0.45 grams of the resin beads. Two mesh sizes, 100-200 and 200-400 were tested. A comparison was made to examine the effect different mesh sizes had on the absorption time of Cr(VI). Water samples were taken at five minute intervals and analyzed by GFAAS. The results are presented in Figure 4.



Figure 4 Kinetics of Cr(VI) Sorption on 100-200 and 200-400 Dowex 1x8 Anion-Exchangers

It took 30 minutes of stirring at a low speed for 100% Cr(VI) sorption to occur on the 100-200 mesh resin and only 20 minutes of stirring for sorption to occur on the 200-400 mesh resin. The data shows that the rate of adsorption was greater for the 200-400 mesh resin then for the 100-200 mesh resin. This result was not unexpected. By having a smaller particle size, the 200-400 mesh resin offers more surface area for the adsorption to take place. However, a decision was made to use the 100-200 mesh resin instead of the 200-400 mesh size. It was found that settling of the finer 200-400 mesh beads after separation took 15-20 minutes while it only took five minutes to settle the 100-200 mesh beads. The added settling time more than negated the faster sorption, therefore, the 100-200 mesh resin beads were selected for further work.

Interferences were tested by adding various amounts of possible interfering ions to the sample. To a 500 ml sample of 50 ppb Cr(VI) in DI water various concentrations of interfering ions were added. The resin was added to the water sample and stirred for 30 minutes. The resin was filtered off and the filtrate tested by GFAAS to see if any Cr(VI) remained in the filtrate due to displacement by the interfering ions. Table 10 shows the effect the added anions had on the sorption of Cr(VI) on the resin beads.

Added Anion	Conc. of Added Anion (ppm)	% Recovery of Cr(VI)
Cl	250	100
HCO ₃	250	99
H ₂ PO ₄	50	102
NO ₃	50	98
SO ₄ ⁻²	25	99
SO ₄ ⁻²	50	96
SO ₄ ⁻²	100	93
SO_4^{-2}	150	92
SO ₄ ⁻²	200	91

Table 10Effect of Common Anions on the Sorption of Cr(VI) on Dowex 1-8x AnionExchange Resin (100-200 mesh)

It was found that Cl, HCO_3 , NO_3 , and H_2PO_4 did not interfere in the quantitative sorption of Cr(VI) at concentrations normally found in tap or groundwaters. In addition, the resin was more tolerant to sulfate than the anion-exchange membrane. Concentrations of up to 200 ppm SO_4^{-2} can be tolerated with use of the resin, while sulfate concentrations above 30 ppm interfered with complete sorption of the Cr(VI) on the doubled membranes.

The natural water samples, spiked with Cr(VI) were also tested with the anionexchange resin. To a 500 ml water sample, 50 ppb Cr(VI) and 0.45 grams of resin was added. The samples were mixed for 30 minutes. The resin was then filtered off and the filtrate analyzed by GFAAS to see if any of the Cr(VI) remained in the solution. It was found that 100% sorption was achieved for all of the natural water samples, including those with the high sulfate concentrations.

The effect of pH was also examined. The pH of standards containing 50 ppm Cr(VI) were adjusted by the addition of HCl or NaOH. The resin was added and the solution was stirred for 30 minutes. The resin was filtered off and the concentration of Cr(VI) was determined in the filtrate by GFAAS. Table 11 shows the results of these test.

рН	% Sorbed
3.5	85
4.0	96
7.0	99
9.9	97

 Table 11 Effects of pH on Sorption

At a pH below 4, the sorption of Cr(VI) was slightly hindered. This was thought to be caused by the conversion of the Cr(VI) to chromic acid, which would have a lesser affinity for the anion-exchange membrane. Approximately 100% adsorption on the anionexchange resin occurred in the pH range of natural water. A normal pH variation in tap water and groundwater has little effect on the anion-exchange resin for Cr(VI) analysis.

4.6 Reaction with DPC and Colorimetric Measurement

After the Cr(VI) had been sorbed on the resin, the beads were separated from the water, rinsed with DI water and added to 10 ml of the 0.04% DPC in acetone solution. It was observed that a rose color developed on the resin. In contrast to the membrane method, the color remained on the resin, and no trace of color was observed in the solution. Tests were performed to determine how long the resin needed to be soaked in the DPC/acetone solution for the color to be fully developed. To 500 ml of a 50 ppb Cr(VI) standard, 0.45grams of the resin was added. The solution was stirred for 30 minutes, filtered, rinsed, and added to 10 ml of the DPC/acetone solution. At various time intervals, a sample of the beads was removed from the solution and their absorbance was measured by SPS using a 1 mm cell. Table 12 shows the results obtained from this experiment.

Time of reaction	Trial 1	Trial 2
(minutes)	Absorbance Readings at 550 nm	Absorbance Readings at 550 nm
5	0.050	0.038
10	0.200	0.205
15	0.442	0.420
20	0.523	0.535
25	0.585	0.589
30	0.585	0.588
35	0.586	0.589

Table 12Kinetic study of Color Development on Anion-Exchange Resin after Sorption
of 500 ml of 50 ppb Cr(VI) and Treatment with DPC/Acetone Solution

From these results, it is clear that 25 minutes is required for the complete reaction to occur between the Cr(VI) and the DPC on the resin. The next facet studied was the packing of the cuvettes with the resin. A test was developed to determine how long it took for the resin to settle and become uniformly packed in the cuvette. The resin was transferred into a 1mm cuvette cell. The cell was placed into the spectrophotometer and the absorbance readings were taken at different time intervals. The data is listed in Table 13. The data shows that within five minutes, the beads have settled to 95% of their final density and that after 25 minutes, no further change occurs.

Absorbance
@ 550 nm
0.300
0.320
0.320
0.330
0.340
0.345
0.350
0.350
0.360
0.360
0.360
0.360

Table 13 Settling of Ion Exchange Beads in 1 mm Cuvette as measured by Absorbance

Standards containing 5, 10, 25, and 50 ppb Cr(VI) were prepared by dilution of the purchased 1000 ppm standard solution with DI water. The portable colorimeter was calibrated by carrying 500 ml portions of the standards through the analysis procedure. After sorption for 30 minutes with occasional shaking, the beads were separated from the water and treated with 10 ml of the DPC/acetone reagent. After color development, the beads were transferred to a 1 mm cuvette, allowed to settle and their absorbance was determined at 550 nm, using the portable colorimeter. Table 14 shows the average absorbance and standard deviation for three replicate measurements.

Cr(VI) (ppb) Average Absorbance		% Standard Deviation	
5	0.064	7.8	
10	0.119	3.9	
25	0.297	5.7	
50	0.589	4.2	

Table 14 Absorbance of Cr(VI) Solutions on Dowex 1-8x Anion Exchange Beads

The natural water samples were also spiked with known concentrations of Cr(VI) and carried through the procedure. The results obtained are presented in Table 15.

Cr(VI) added	Flanders Water	Newark Water	Green Twp.	Effort Water
(ppb)			Water	
5	6.8	4.0	5.2	7.0
10	10.9	8.6	13.2	10.1
25	22.8	28.0	25.8	29.4
50	55.2	48.5	51.9	45.4

 Table 15
 Cr(VI) Recovery from Fortified Natural Water Samples after Preconcentration on Dowex 1-8x Resin

From the data collected, it can be concluded that the sensitivities of the methods using anion exchange membranes or ion exchange beads are similar. Concentrations of Cr(VI) in the range of 2 - 50 ppb can be measured. The method using the Dowex 1-8x beads is less sensitive to sulfate interference. The ion exchange capacity of the Dowex 1-8x is about 1.2 meq/g. For 0.45 grams of resin used in each determination, the capacity is about 26 mg of sulfate ion This corresponds to a concentration of 52 ppm sulfate in a 500 ml water sample. Since the sorption of Cr(VI) is complete at much higher amounts of sulfate, there must be a preferential sorption of Cr(VI) in this system. This is confirmed by the use of strongly basic anion exchangers for removal of chromate from cooling waters in the presence of sulfate. ³¹

The accuracy and reproducibility of the determination using the beads and SPS is lower than that by the membrane method, but it is acceptable for most environmental applications at the low ppb level. There are no major difficulties in carrying out the SPS method in the field, although the membrane method is preferred as it is both faster and more accurate, when sulfate levels are sufficiently low. The colorimeter may be standardized in the laboratory before field measurements are to be made. Also, standard solutions may be preconcentrated on the beads or membranes in the laboratory, and the final steps in the analysis carried out in the field, to produce an on-site calibration check. No difference in final concentration was found when Cr(VI)-loaded beads were stored in plastic bags for up to seven days before color development with DPC and measurement, in comparison with beads which were treated immediately after preconcentration was completed.

4.7 Field Screening Method for Cr(VI) in Water

The method using the Dowex 1-8x beads can be adapted for an on-site screening test. The preconcentration step is carried out in a plastic bottle using 0.45 grams of resin beads, and 500 ml of sample. After the water is squeezed out of the bottle, the beads retained in the cap are rinsed with DI water, and 5 ml of DPC reagent is added. The color gradually develops on the beads. (Figure 5)


Figure 5 Color Developed on Anion-Exchange Resin

After 20-25 minutes the colors are matched with a color scale produced in the laboratory. (Figure 6) The color scale was made by carrying standards at 0, 5, 10, 25, and 50 ppb through the analysis, and matching the colors, using acrylic paints. The colors ranged from yellow for the blank through peach and pink to purple for 50 ppb. Each of the standard solutions gave an easily distinguishable color. The color scale is shown on Figure 6.



Figure 6 Color Scale for Field Screening Method

It should be noted that the colors reproduced above are somewhat different from the actual colors, because of the photographic and reprodecing technologies. However, the relative color differences due to the changes in Cr(VI) concentrations are easily seen.

CHAPTER 5

ANALYTICAL PROCEDURES DEVELOPED IN THIS PROJECT

In this project, three different variants of the determination of Cr(VI) at low ppb levels in fresh water were developed. These are:

- A rapid and portable method, preconcentrating the Cr(IV) on a membrane and extracting it for colorimetric measurement. This method is suitable for samples which are low in sulfate.
- A portable colorimetric method for Cr(VI) in water using a hand-held spectrometer and SPS.
- A non-instrumental field screening test for Cr(VI) in water.

All these methods are quite specific to Cr(VI), and are useful in the low ppb range of concentrations. The only significant interference found has been high amounts of sulfate, which will give low results with the membrane method. A detailed description of these methods are given in this section.

All Three Methods Require:

• DPC reagent: This was prepared by dissolving 500 mg of DPC in 25 ml of acetone. Two ml of the DPC/Acetone solution was then transferred to a 100 ml flask containing 10 ml of 1 M H₂SO₄. The flask was filled to the mark with DI water. The reagent was prepared fresh each day and stored in a brown bottle.

- 1000 ppm BaCl₂ adjusted to a pH of 2 with HNO₃. This solution is used for the sulfate screening test, to determine which method is suitable for the particular site.
- DI water.
- 5 and 10 ml measuring pipettes.
- 0.45 μm filter and membrane filter holder (Millipore Swinnex-47) for initial filtration of turbid samples.

For the Membrane Method:

The following additional equipment is required:

- Portable colorimeter (Mini-20, Fisher Scientific) with 10 mm cuvettes.
- SS-6407 anion-exchange membrane filters (Gelman) and suitable holder.
- 100-200 ml plastic syringe.
- 10 ppm Cr(VI) standard solution, for on-site calibration check.

For the SPS Method using Anion Exchange Beads:

The following equipment is required:

- Portable colorimeter (Mini-20, Fisher Scientific) with 1 mm cuvette.
- Pre-weighed 0.45 grams portions of Dowex 1-8x anion exchange resin packed in plastic bags or placed in the bottles to be used for sample treatment.

- Similar portions of ion exchanger, pre-loaded with Cr(VI), to be used for on-site calibration check.
- Plastic bottles fitted with caps which allow the water to be removed while retaining the beads. Bottles should have sufficient capacity to contain 500 ml samples with room for shaking, and caps should be sufficiently large to contain beads and 5 ml of reagent solution.

For the Field Screening Test:

- Pre-weighed 0.45 grams portions of Dowex 1-8x anion exchange resin packed in plastic bags.
- Plastic bottles fitted with caps which allows the water to be removed while retaining the beads. Bottles should have sufficient capacity to contain 500 ml samples with room for shaking
- Color matching chart.

5.1 Sulfate Screening Method

Before applying the Cr(VI) membrane or bead pre-concentration methods, the water sample is tested for sulfate content. Ten ml of a 1000 ppm BaCl₂ solution, adjusted to pH 2 with nitric acid, was added to 10 ml of a water sample. The mixture was shaken for one minute and allowed to stand for five minutes. The turbidity of the solution was examined by eye. If no turbidity is observed, the sulfate concentration is below 15 ppm and the membrane method can be used. If the turbidity is slight, the test is repeated using 5 ml water, 5 ml DI water and 10 ml of BaCl₂. If this test is clear, then a double membrane can be used. Otherwise the anion exchange bead method should be used. If the precipitate is voluminous and rapid, it is recommended that the sulfate level be checked with a standard method before the results of the Cr(VI) tests are used.¹³

5.2 Method for Determination of Cr(VI) in Fresh Water which is Low in Sulfate Using Preconcentration on a Membrane

This method is useful for tap water, groundwater and surface water in which the sulfate concentrations do not exceed 25 ppm. A simple classification test for sulfate was described above, or a standard method may be used. If the sulfate concentration is between 15 and 25 ppm a double membrane should be used. Below 15 ppm a single membrane is sufficient. If the sample water is turbid, it should be filtered through a 0.45 μ m filter before analysis.

Place one or two SP6407 membrane filters into a holder and using a 100 ml syringe pass the entire 100 ml of the sample through the membrane. This takes approximately four minutes to complete. Remove the membrane from the holder and immerse it in 5.0 ml DPC reagent solution (0.04% in acetone, with the pH adjusted to 2). Stir or shake gently from time to time. After four minutes, decant the liquid into a 1 cm glass cuvette, and measure the absorbance at 550 nm. DI water is used to zero the instrument.

Calibration is carried out by taking standard solution of Cr(VI) and treating these in the same manner as the samples. Calibration of the colorimeter can be done in the laboratory before taking it to the field. For added assurance of accuracy, a field standard should be done, by bringing a 100 ml of standard Cr(VI) solution, or a previously loaded membrane to the field and running that along with the samples.

5.3 SPS Method for Determination of Cr(VI) in Fresh Water at Low ppb Levels This method is applicable to the determination of low ppb levels of Cr(VI) in tap, ground or surface waters having sulfate concentrations below 150 ppm. The determination is carried out using a plastic bottle fitted with a filter paper-lined cap, with a hole in the top of the cap. This hole is sealed by a snap-top (Heinz ketchup bottles and caps were used in this project). A 0.45 grams portion of 100-200 mesh Dowex 1-8x anion resin is weighed into the bottle before taking it to the field. A measured volume of 500 ml of the water sample is poured into the capped bottle. The bottle can be stirred mechanically at slow speed for 30 minutes, or can be hand shaken for two minutes followed by three minutes standing. The hand shaking is repeated until 30 minutes have elapsed.

After the sorption is completed, the snap-top is opened and the water is discarded through the filter by squeezing the plastic bottle. The anion exchange resin beads are collected in the cap, and the snap-top is closed. A 5 ml portion of 0.04% DPC reagent is added to the cap and is stirred into the beads. After 20 minutes of reaction time, the beads are transferred with a dropper to the 1 mm cuvette, and allowed to settle. A cuvette containing non-reacted beads slurried in water was used as a blank. The sample and blank were analyzed at 550 nm and compared to readings taken at 700 nm to ensure uniform packing..

For calibration, 500 ml portion of standard solution of Cr(VI) at various concentrations can be sorbed onto the resin beads. Before developing the color with

DPC, the beads can be packed and taken to the field. There they can be developed and run along with the samples.

If the sulfate concentration of the samples is above 150 ppm, interference is possible. In this case a smaller sample should be taken for analysis. However, this will raise the detection limits somewhat.

5.4 Field Screening Test

Water samples, 500 ml are mixed with 0.45 grams of Dowex 1-8x anion exchanger beads in the same plastic bottles described above. The sorption process is carried out as above. After 5.0 ml of 0.04% DPC/acetone reagent is added to the beads contained in the bottle cap, the color is allowed to develop for 25 minutes. Then the colors are compared by eye with a previously prepared color chart. A scale was prepared with distinctly differentiable colors for each concentration: 0, 5, 10, 20, 35, and 50 ppb.

CHAPTER 6

CONCLUSION

In this project, three colorimetric methods were developed for the determination of Cr(VI) in fresh waters. They are accurate down to the low ppb range. These methods were tested with standard solutions in distilled water and with fortified tap water and groundwater from several sources.

For samples which have low sulfate concentration, below 25 ppm, the use of an anion exchange membrane for separation and preconcentration of Cr(VI) was tested. The Cr(VI) was absorbed on the anion exchange membrane by passing the water sample through single or double membranes. The sorbed Cr(VI) was eluted, complexed with DPC and determined by absorbance spectrometry at 550 nm, using a portable colorimeter. The determination takes about ten minutes.

If the sulfate concentration is higher, up to 150 ppm, the Cr(VI) may sorbed on anion exchange beads in a batch process. The beads are separated from the solution, treated with DPC reagent, and are transferred as a slurry into a 1 mm glass cell. The colorimeter may be calibrated in the laboratory before bring it to the field. Each determination requires about 50 minutes, most of which is standing time.

Finally a screening test was developed. The Cr(VI) is sorbed onto the anion exchange beads and the color developed with DPC. After a 25 minutes development time, the color of the beads is compared with a previously prepared color chart.

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These methods are about 20 times more sensitive than the standard colorimetric DPC method for Cr(VI) in solution. Interference from cations such as Fe(III) and Cu(II) which affect the standard method are eliminated. The accuracy of the membrane method is similar to that of the standard colorimetric method. The accuracy of the method using beads and SPS is slightly lower, but adequate for most applications at the low ppb level.

These methods are simple, inexpensive and suited to on-site use by nonprofessionals after minimal training. The necessary equipment, the colorimeter, plastic ware, and reagents fit easily into a small carrying case.

Future work in this field will include the examination of newer, more selective membrane materials as these become available, as well as, other ion exchange materials which may prove useful in the determination of Cr(VI) and other toxic metals in environmental water samples, a field kit for the determination of Cr(VI) at low ppb levels in fresh water may be developed. The application of these methods to extracts of solid samples containing low concentrations of Cr(VI) is another area which should prove fruitful in future work.

CHAPTER 7

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